MATRIX-ISOLATION INFRARED SPECTROSCOPIC STUDIES OF $CINO_x$

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ABSTRACT

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MATRIX-ISOLATION INFRARED SPECTROSCOPIC STUDIES OF $ClNO_x$

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The matrix-isolation infrared spectroscopic studies of the gas-phase reactions of nitrogen dioxide with chlorine atoms indicate the formation of two isomers. The products of this reaction are $ClNO_2$ (1696 cm^{-1}) and ClONO (1719 cm^{-1}). The variable pathlength study shows that in the gas-phase these two isomers are not produced in equal quantities and that the isomer $ClNO_2$ is more stable than ClONO.

The matrix-isolation infrared studies of synthetic chlorine nitrate is investigated. Two chlorine nitrate isomers ($ClONO_2$ and ClOONO) are identified.

The gas-phase reaction study of nitrogen dioxide with ClO, was performed. Chlorine monoxide used in these reactions was generated by the reactions (a) $Cl_2O + Cl \longrightarrow ClO + Cl_2$; (b) $Cl + O_3 \longrightarrow ClO + O_2$. The observed products of this reaction are $ClONO_2$ and ClOONO. Comparison of the spectra with the matrix-isolated

spectra of synthetic chlorine nitrate coupled with isotopic study helped us to assign the vibrational peaks of $ClONO_2$ (1727, 1286, 808, 784, 558, 423, and 270 cm^{-1}) and ClOONO (1736, 1719, 1417, 924, 849, 558, 448, and 443 or 414 cm^{-1}) isomers. The relative stability of these two observed isomers as related to the chlorine and nitrogen oxide catalytic cycles in the depletion of stratospheric ozone is discussed.

TABLE OF CONTENTS

CHAPTER II

CHAPTER III

INTRODUCTION

Recently, much interest has been shown in the gas-phase reaction mechanism of chlorine atoms in various catalytic cycles and the effect they have on the concentration of ozone in the stratosphere. Many authors have proposed that certain pollutants, especially those of chlorine and nitrogen oxides, deplete the stratospheric ozone layer.[1-3]

The stratospheric ozone layer filters out high energy ultraviolet radiation (2000-3800 Å) from the sun. Ultraviolet radiation at wavelengths below 210 nm dissociates oxygen molecules to produce oxygen atoms (1) which then combine

$$O_2 + h\nu \xrightarrow{210\ nm} 2O\ (^3P) \qquad (1)$$

with oxygen molecules to form ozone (2).[4]

$$O + O_2 \longrightarrow O_3 \qquad (2)$$

There are certain basic reactions of stratospheric ozone, among which are the following:[3,5,6]

$$O_2 + h\nu \longrightarrow 2O \qquad (1)$$

$$O_3 + h\nu \xrightarrow{310\ nm} O(^1D) + O_2 \qquad (3)$$

$$M + O_2 + O \longrightarrow O_3 + M \qquad (4)$$

$$O_3 + O_2 \longrightarrow 2O_2 + O \qquad (5)$$

It is clear that the most important reactions above are reactions (3) and (4), as these indicate a steady-state concentration of stratospheric ozone.

$$O_3 + h\nu \longrightarrow O_2 + O \qquad (3)$$

$$M + O_2 + O \longrightarrow O_3 + M \qquad (4)$$

$$M + O_3 \longrightarrow M + O_3 \ (\text{net})$$

Reaction (3) is initiated by the absorption of high energy ultraviolet radiation which is harmful both ecologically and physiologically. However reaction (4) ensures the steady-state concentration of ozone. The presence of aerosols (CF_xCl_y, Cl_2, nitrogen oxides) provides possible sinks for stratospheric ozone, thereby leading to the depletion of its concentration.

The chlorine oxides (ClO_x) are examples of such sinks. The stratosphere is polluted in several ways by chlorine. The two most important sources of it are from the diffusion of freons (CF_xCl_y) from the troposphere and from the by-products (in

the form of HCl) of exhaust from space shuttles. Both the freon and hydrochloric acid are photolytically dissociated to give chlorine atoms,

$$CF_3Cl + h\nu \longrightarrow CF_3 + Cl \qquad (6)$$

$$HCl + h\nu \longrightarrow H + Cl \qquad (7)$$

This is achieved after diffusion into the stratosphere. The chlorine atoms may then catalytically destroy ozone molecules by the following mechanism:

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (8)$$

$$ClO + O \longrightarrow O_2 + Cl \qquad (9)$$

$$O_3 + O \longrightarrow 2O_2 \quad \text{(net)}$$

Since the chlorine atom is not used up, reactions (8) and (9) exemplify catalysis. By estimation, each chlorine atom present in the stratosphere destroys about 10,000 molecules of ozone.[7]

Likewise, NO_2 is photolytically dissociated to give NO molecules

$$NO_2 + h\nu \longrightarrow NO + O \qquad (10)$$

which can also destroy ozone molecules in the following reactions:[8]

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad (11)$$

$$NO_2 + O \longrightarrow NO + O_2 \qquad (12)$$

$$O_3 + O \longrightarrow 2O_2 \quad \text{(net)}$$

Reaction schemes for gas-phase reactions of chlorine in the stratosphere have been proposed by Stolarski and Cicerone (SC), and they have shown, according to their reaction scheme, that chlorine concentrations of 1 ppb may result in significant ozone depletion.[9]

Wofsy and McElroy[10] and Molina and Rowland[11], have also proposed that chlorine oxides may constitute an important catalytic sink for ozone. Recently Yung, Pinto, Watson and Sander proposed that trace concentrations of bromine oxides (BrO_x) are also involved in the catalytic destruction of ozone.[12] Nitric oxides (NO_x) also constitute sinks for stratospheric ozone.[10]

However, the role of the reactions:

$$Cl + NO \longrightarrow ClNO \qquad (13)$$

$$Cl + NO_2 \longrightarrow ClNO_2 \qquad (14)$$

and reactions:

$$ClO + NO \longrightarrow ClONO \qquad (15)$$

$$ClO + NO_2 \longrightarrow \text{Products} \qquad (16)$$

as possible sinks for both odd chlorine and nitrogen species in the stratosphere chemistry has been proposed.[13,14]

In this thesis, the technique of matrix-isolation is employed to study the reaction products of chlorine atoms with NO_2, chlorine atoms with Cl_2O and NO_2, and chlorine atoms with ozone and NO_2.[15-17] The reactions are carried out in the gas-phase and reaction products are trapped at 10K, and characterized by their infrared spectra.[18-20] The feasibility of employing the relatively well known matrix-isolation technique to trap intermediates and products of gas-phase reactions in order to gain information about the mechanisms of these reactions has been shown.[21,22] The application of this technique is unique in that the reactants are mixed in a gas-phase kinetic cell of variable pathlength. The products are subsequently isolated in an inert gas matrix and spectroscopically identified. Since reactions studied are correctly gas-phase reactions and not matrix reactions, the results obtained may then be directly extrapolated for use in the atmospheric modeling.

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CHAPTER I

A STUDY OF THE GAS-PHASE REACTIONS OF CHLORINE ATOMS WITH NITROGEN DIOXIDE

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

The ClO_x and NO_x stratospheric ozone depletion chain reaction mechanisms are well known. The ClONO species, in particular, has been invoked as a product of the chain termination step in the chlorine oxide and nitrogen oxide depletion schemes.[1]

$$ONO + Cl \longrightarrow ClONO \quad (1\text{-}1)$$

$$ClO + NO \longrightarrow ClONO \quad (1\text{-}2)$$

Many workers have found the matrix-isolation technique particularly well suited to the study of halogen atom chemistry.[2-7] Earlier studies of the matrix reactions of fluorine atoms with NO_2 produced the 'hypofluorite' form FONO of nitryl fluoride.[8,9] This suggested the possible synthesis of ClONO intermediate by analogous reactions between chlorine atoms and NO_2 (1-3).

$$Cl + NO_2 (+M) \longrightarrow \text{Products} \quad (1\text{-}3)$$

The products of reaction (1-3) are reported to be ClONO (~ 80%) and $ClNO_2$ (~ 20%).[10] Recent theoretical studies by Chang et al explains the preferential formation of ClONO.[11] However matrix reaction studies by Tevault and

Smardzewski indicate that $ClNO_2$, ClONO and OClNO are the products of reaction (1-3).[12]

In this work, experimental results also indicate formation of ClONO and $ClNO_2$ but in ratios different from what has been observed before.

EXPERIMENTAL

A low temperature (10K) necessary for the matrix-isolation was obtained and maintained by means of an Air Products Cryotip and helium refrigerator (model CSA-202). The cryotip has a rotatable section with an optical port, designed to provide the flexibility for infrared spectroscopic studies (Fig. 1-1). A quartz kinetic reaction cell (Fig. 1-2) of variable reaction pathlength, 3-35 cm, attached ensures that reactions take place in the gas-phase prior to deposition on the cold CsI window.

The infrared spectra (4000-200 cm^{-1}) were recorded using a Beckman 4250X spectrometer, with a resolution better than 1 cm^{-1} in the areas of interest. The spectrometer was interfaced with a MINC 11 microcomputer, with all spectra digitally recorded and analyzed using our software.

Prior to each experiment, the cryogenic cell (Fig. 1-3), the CsI windows, and the quartz reaction cell were thoroughly cleaned. The stainless steel cryogenic cell was first cleaned using CCl_4 to remove any grease films that might have accumulated in the previous experiment. The acetone was used to remove the CCl_4, and finally 200 proof ethanol was used to remove the acetone. The O-rings were cleaned and greased using high vacuum grease. The cryogenic system and the quartz kinetic cell were first pumped on using a mechanical pump until pressure read 10^{-1} torr. Then they were pumped on by an oil diffusion pump overnight to further remove volatile compounds and water. Typical pressure in the evacuated reaction cell was 10^{-5} - 10^{-6} torr.

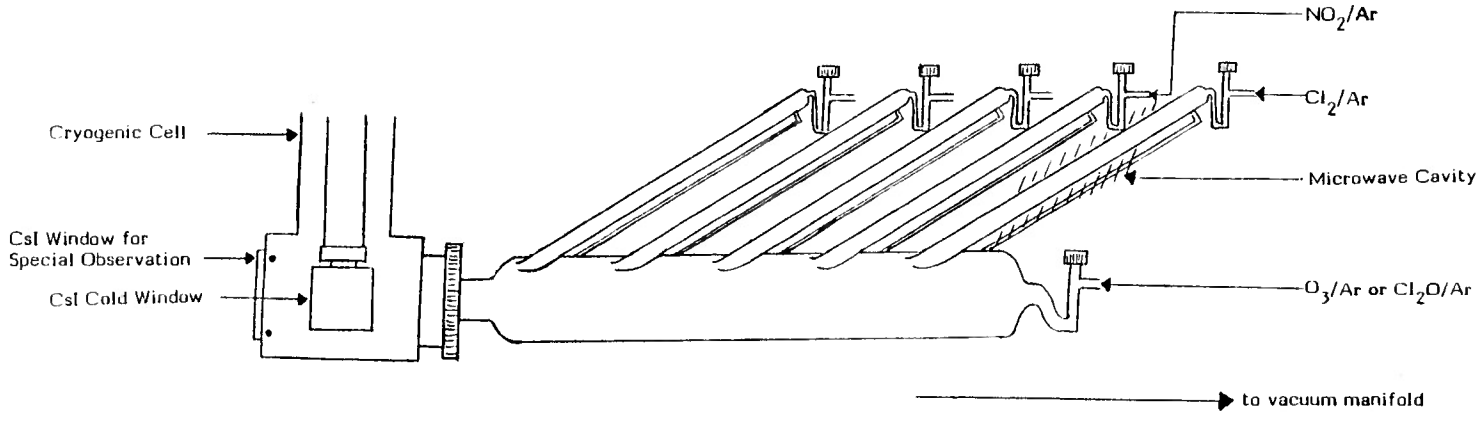

Fig. 1-1. Schematic of experimental apparatus.

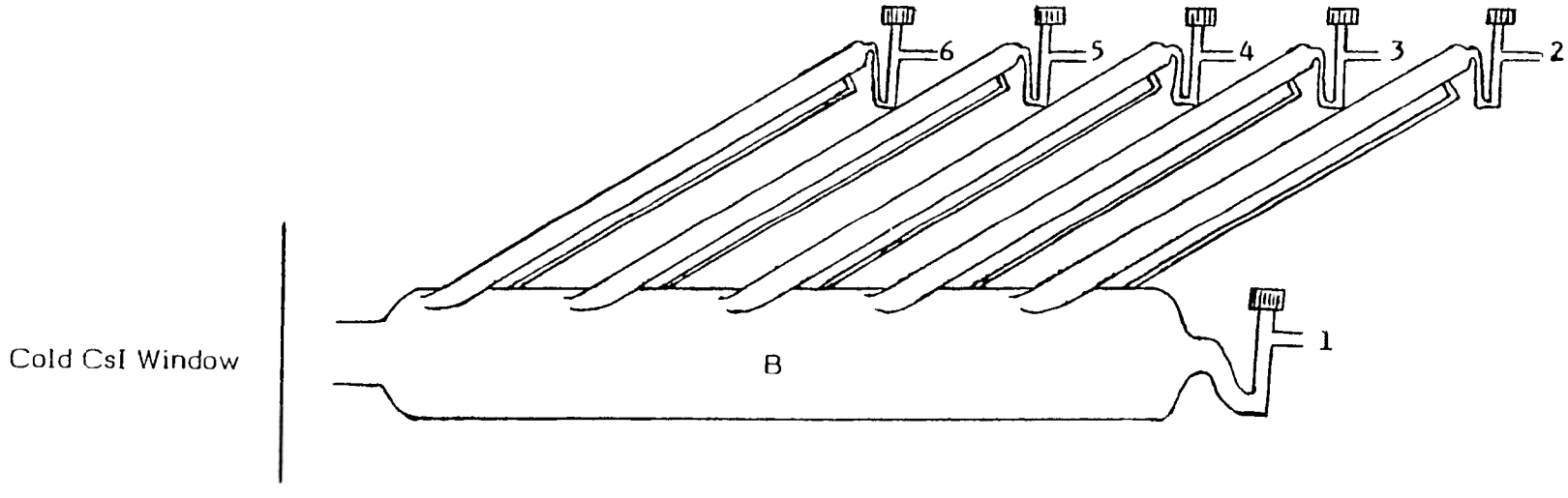

Fig. 1-2. Quartz reaction cell. 1-6 are the inlets.

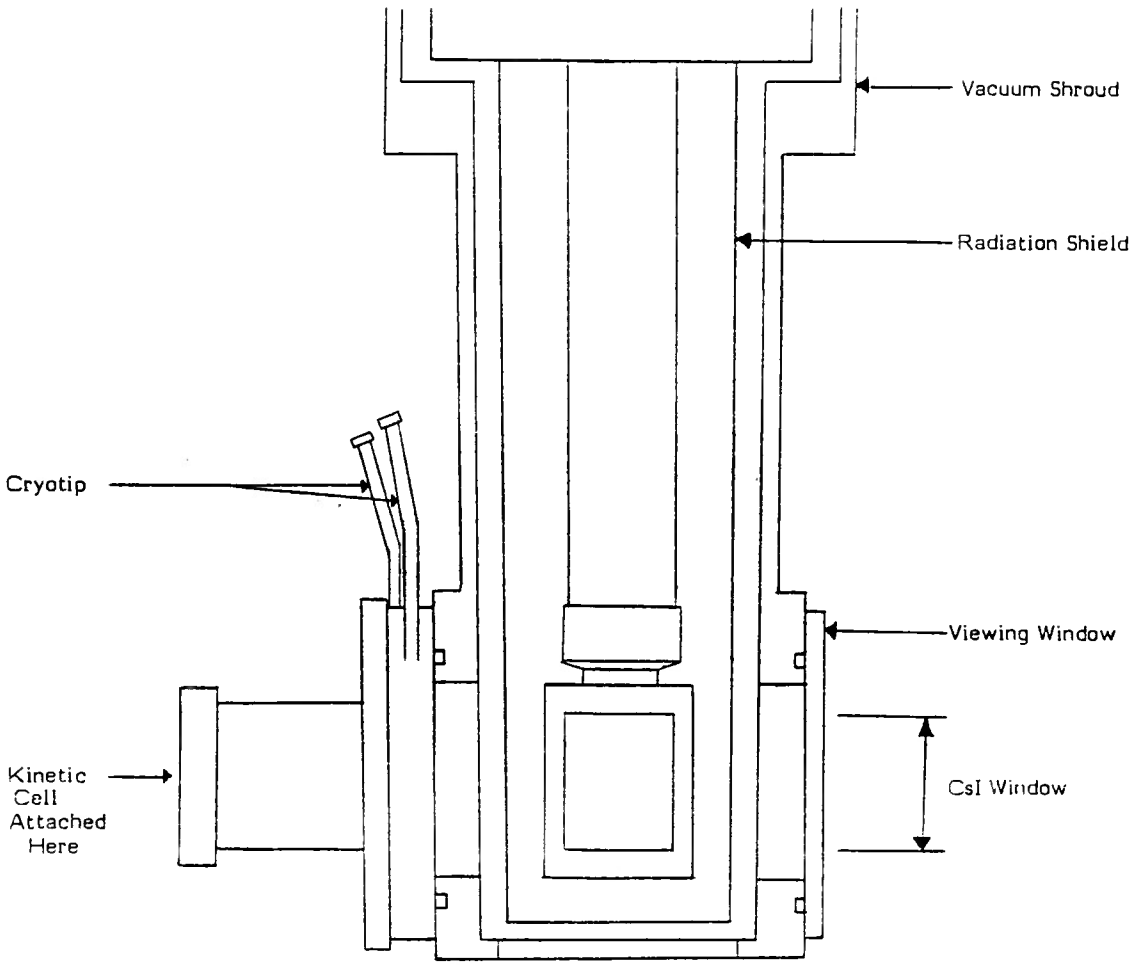

Fig. 1-3. Cross-section of cryogenic cell.

The CsI windows were thoroughly cleaned using a lintless, leather polishing cloth moistened with 200 proof ethanol for 20-30 sec. The window was polished on a dry section of the leather cloth for another 10-15 sec. This procedure was repeated 2 to 3 times or until the window was transparently clean. Any scratch on the window was removed by grinding on a 200-grit sandpaper, and then on 600-grit sandpaper to remove scratches due to the courser paper. After the grinding the window was polished using the above method. It was necessary to take this care so as to achieve maximum infrared transmittance and to avoid any unwanted reactions taking place with impurities on the CsI windows. Background spectra of the cleaned evacuated system were always taken to ensure that no impurities were left on the rectangular CsI window.

The kinetic cell was thoroughly cleaned prior to each experiment, first with hydrofluoric acid, followed by deionized water, and finally with 200 proof ethanol. It was necessary to do this to prevent products of microwave discharge used in the production of chlorine atoms from reacting with the glass walls of the kinetic cell. Hydrofluoric acid also prevents recombination of chlorine atoms on the walls of the cell.

Molecular chlorine (Matheson Gas Products, 99.9%) was purified by trap to trap distillation at 77K. Chlorine atoms were produced by microwave discharge of Ar/Cl_2 mixtures using a Kiva Corp. microwave discharger operating at 50 watt power. Reflected voltage was always adjusted to zero so as to ensure the same amount of power incident on the quartz tube. Other excited species are probably produced; for example Cl_2^+, Cl_2^-, Cl^-, Ar^+, Ar^* (excited argon) and $ArCl_x$.[13,14] The

products of the discharge when mixed with ozone or oxygen may produce species like ArO_x. In this work, $ArCl_x$, ArO_x and Ar* species, if formed, would interfere with experimental interpretations. The ArO_x and $ArCl_x$ are unobservable in this system and it is only excited argon that can cause unwanted side reactions as it reacts with oxygen to produce ozone through the proposed mechanism:[15,16]

$$Ar^* + O_2 \longrightarrow Ar + 2O \qquad (1\text{-}4)$$

$$O + O_2 \longrightarrow O_3 \qquad (1\text{-}5)$$

$$Ar^* + 2O_2 \longrightarrow O_3 + O + Ar \text{ (net)}$$

In the study of this system we performed experiments in which: (1) argon was passed through the microwave discharge and the excited argon produced was reacted with O_2 to determine if reactions (1-4) and (1-5) are gas-phase; (2) O_2 was first deposited on the cold CsI window and Ar* was allowed to react with the deposited O_2 to determine if the reactions were matrix reactions; and (3) argon was discharged on different sides of the kinetic cell in order to determine if the Ar* was dissociating O_2, or whether the light from the microwave discharge was dissociating the O_2.[15] However O_3 was produced no matter which side of the kinetic cell argon was discharged. This eliminated the possibility of light from the microwave discharge entering into the reaction. Also O_3 was produced both in the gas-phase and by reaction on the matrix.

Therefore, it means there is no way of eliminating Ar* as long as microwave discharge is used to produce chlorine atoms. It should be noted, however, that discharge of Ar/x mixtures is widely used to produce free radicals.

Nitrogen dioxide (Matheson 99.9%) was first purified by cooling in an ethanol/dry ice slush (201K). Impurities (NO and N_2O_3) condensed as a blue solid while NO_2 and N_2O_4 remained in the gas-phase. Infrared observations of the purified sample showed absorptions at 1876 cm^{-1} attributed to NO. Further purification was carried out by reintroducing NO_2 along with O_2 into a 5-dm^3 flask in a ratio of 2:7. The gas mixture was allowed to stand for 48 hr at 298K and 1 atm. This converted NO into NO_2 by the thermal reaction:

$$2NO + O_2 \longrightarrow 2NO_2 \qquad (1\text{-}6)$$

The gas mixture was freeze-thaw degassed at dry-ice and liquid nitrogen temperatures to eliminate O_2.[17] The purified product was a white solid (NO_2) with infrared absorption at 1617.6 cm^{-1}. In all of the experiments Cl_2/Ar (1:50) was allowed to react with NO_2/Ar (1:200). The points of introduction were varied starting with NO_2/Ar in inlet 1 and Cl_2/Ar in inlet 2 (Fig. 1-2). This varied the reaction pathlength from 35-12.5 cm. In each experiment 2.72 X 10^{-4} mmoles of Cl_2 was reacted with 0.694 X 10^{-4} mmoles of NO_2 to ensure the same sample size. The Cl_2/Ar microwave discharge was started first and NO_2/Ar mixture flow was started after the discharge was stabilized. The chlorine atoms this produced were allowed to react with NO_2 in the reaction cell region B (Fig. 1-2), and the products formed were deposited on the rectangular CsI window which was precooled to 10K. Deposition time ranged from 1.05-1.33 hr. Infrared spectra of the samples were recorded using the Beckman 4250X spectrometer described earlier.

RESULTS AND DISCUSSION

A typical spectra obtained from the gas-phase reaction of chlorine atoms and nitrogen dioxide is shown (Fig. 1-4). The observed vibrations are listed in Table 1-1. The absorptions at 1617.6 cm^{-1} and 749.4 cm^{-1} are observed in NO_2/Ar spectra. These absorptions are assigned to NO_2 molecules, while the peaks 1288.2 cm^{-1} and 1245.7 cm^{-1} are assigned to N_2O_4.[18] The peak at 1876.9 cm^{-1} is assigned to NO. This absorption is also observed when the microwave discharge argon (Ar*) and NO_2/Ar are simultaneously deposited at 10K.[12] The NO_2 used in these experiments was purified as described earlier, hence the NO in the experimental set up is due to nitrogen which is an impurity (~ 5 ppm) in the argon used. Peaks at 1781.9, 1719.4, 1695.7, 1680.0, 1320.7, 1267.6, 836.9, 786.9, 649.4, 413.8, 399.4 and 360.0 cm^{-1} (Table 1-1) are attributed to the products formed from chlorine atoms and nitrogen oxides. To ensure that the above peaks are indeed due to the gas-phase reaction of chlorine atoms and nitrogen oxides, two sets of experiments were performed. In the first set of experiments, Cl_2/Ar (1:50) and NO_2/Ar (1:300) mixtures were codeposited, and the only peaks observed in the infrared spectra are those due to NO_2 and N_2O_4. The above mentioned absorptions were not observed. Thus the possibility of these absorptions arising from the reaction of Cl_2 with NO_2 is ruled out. In the second set of experiments, the NO_2/Ar (1:200) was deposited on the cold CsI window and appropriately discharged Cl_2/Ar (1:50) mixture was deposited on top of the NO_2/Ar mixture. The infrared absorptions are only those due to NO_2 (1617.6 and 749.4 cm^{-1}), N_2O_4 (1288.2 and 1245.7 cm^{-1}) and NO (1876.9 cm^{-1}).

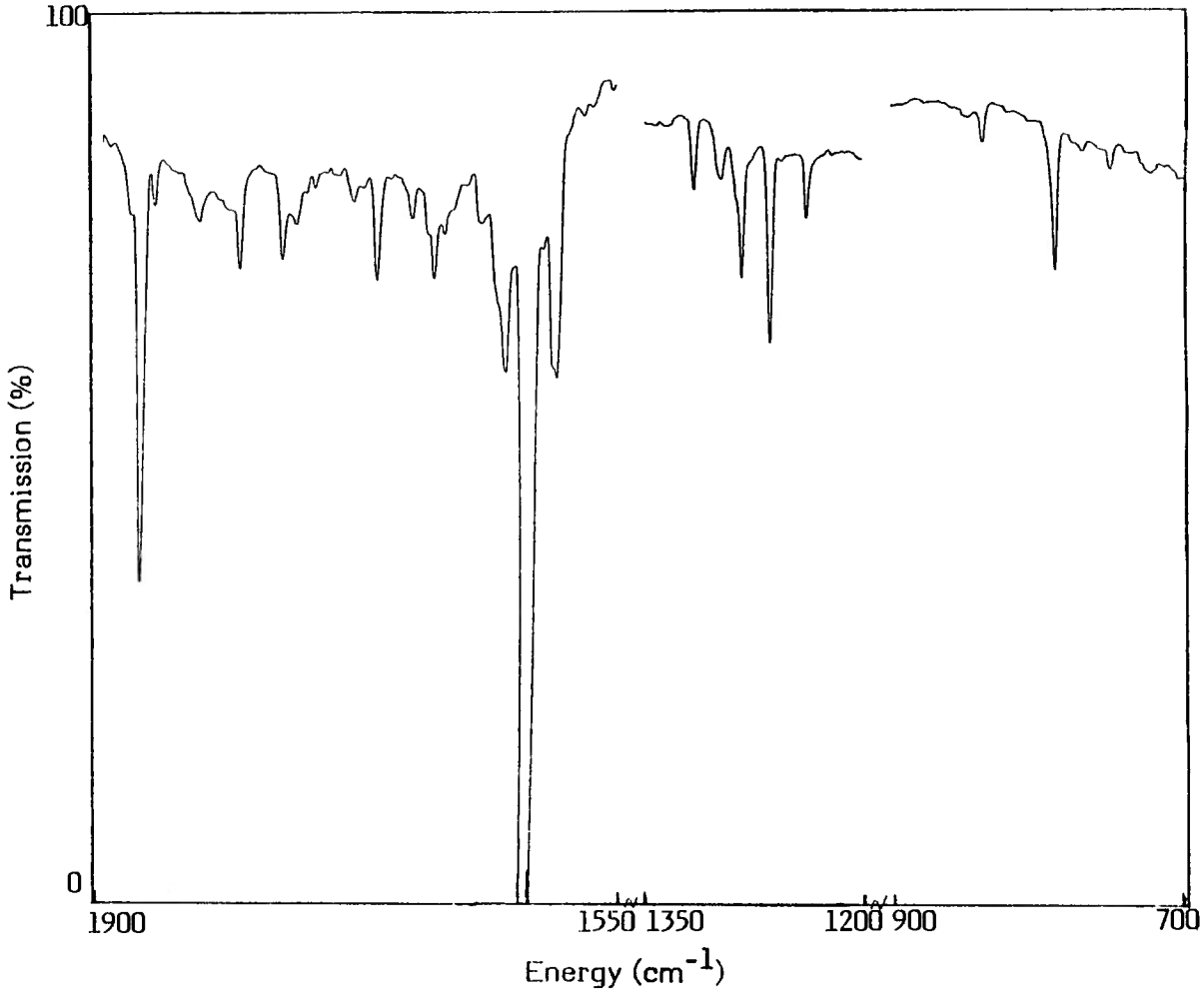

Fig. 1-4. The IR spectra of the gas-phase reaction products of chlorine atoms/argon (1:50) mixtures with NO_2/Ar (1:200) mixtures.

Table 1-1. Infrared Absorptions (cm^{-1}) of the Products from Cl + NO_2 (+M) Reactions in the 4000-200 cm^{-1} Spectral Region.[a]

$$^{14}NO_2 + {}^{35}Cl + Ar^*$$

ENERGY (cm^{-1})	ASSIGNMENT
2213.8	N_2O
1876.9	NO
1811.3	N_2O_4
1781.9	ClNO
1719.4	ClONO
1695.7	$ClNO_2$
1680.1	$ClNO_2$
1617.6	NO_2
1320.7	$ClNO_2$
1288.2	N_2O_4
1267.6	$ClNO_2$
1245.7	N_2O_4
836.9	ClONO
786.9	$ClNO_2$
749.4	NO_2
649.4	ClONO
413.8	$ClNO_2$
399.4	ClONO
386.9	ClONO
360.0	$ClNO_2$
265.0	ClONO

a. Energies are calibrated using CO_2 absorption in matrix at 2338.8 cm^{-1}.

Thus, the possibility of matrix reactions between chlorine atoms and NO_2 and NO are ruled out.

The absorption at 1781.9 cm^{-1} is assigned to ClNO. This assignment is confirmed by $^{15}NO_2$ isotopic shift of 26.2 cm^{-1} (Table 1-2) and is in agreement with published data.[12] This peak is arising from the gas-phase reaction of chlorine atoms with NO (produced by microwave discharge of N_2 present in argon).

Based on published data, the absorptions at 1719.4, 836.9 and 386.9 cm^{-1} are assigned to ClONO.[12,19] This is further confirmed by the isotopic shifts (30.6, 10.6, and 7.5 cm^{-1}) of these absorptions. These isotopic shifts (Fig. 1-5) are also in agreement with the previously reported values.[12,19] The observed infrared absorptions at 1695.7, 1680.1, 1320.7, 1267.6, 786.9, and 360.0 cm^{-1} are assigned to the isomeric form $ClNO_2$. These absorptions and their respective isotopic shifts at 18.1, 12.6, 21.9, 23.8, 11.4 and 8.7 cm^{-1} (Table 1-2) are in close agreement with the work of Tevault and Smardzewski.[12] Thus the products observed in these experiments are ClNO, $ClNO_2$ and ClONO. These products were also observed by other workers.[10,12-20] No peaks were observed around 1752.5 cm^{-1}, which has been assigned to the isomer OClNO by Tevault and Smardzewski.[12] The presence of $ClNO_2$ and ClONO in these experiments confirms the conclusion that the Cl + NO_2 + M reaction follows the two paths proposed by Niki et al.[10]

$$Cl+NO_2+M \xrightarrow{k_{1a}^{11,21}} ClNO_2+M;\ k_{1a} \approx 6.2\times10^{-31} cm^6\ molecule^{-3}\ s^{-1} \quad (1\text{-}7)$$

$$Cl+NO_2+M \xrightarrow{k_{1b}^{11,21}} ClONO+M;\ k_{1b} \approx 30.0\times10^{-31} cm^6\ molecule^{-3}\ s^{-1} \quad (1\text{-}8)$$

Table 1-2. Infrared Absorptions (cm^{-1}) of the Products from Cl + ^{15}NO (+M) Reactions in the 4000-200 cm^{-1} Spectral Region. [a]

$$^{15}NO_2 + {}^{35}Cl + Ar^*$$

ENERGY (cm^{-1})[b]	ASSIGNMENT
2171.3 (42.5)	N_2O
1838.8 (38.1)	NO
1788.8 (22.5)	N_2O_4
1755.7 (26.2)	ClNO
1688.8 (30.6)	ClONO
1677.6 (18.1)	$ClNO_2$
1667.6 (12.55)	$ClNO_2$
1570.7 (46.9)	NO_2
1298.8 (21.9)	$ClNO_2$
1290.6	$ClNO_2$
1278.8 (9.4)	N_2O_4
1243.8 (23.8)	$ClNO_2$
--	--
826.3 (10.6)	ClONO
777.6 (11.4)	$ClNO_2$
741.3 (8.1)	NO_2
379.4 (7.5)	ClONO
351.3 (8.7)	$ClNO_2$
253.2 (11.8)	ClONO
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a. Energies are calibrated using CO_2 absorption in matrix at 2338.8 cm^{-1}.

b. Isotopic shifts are in parenthesis.

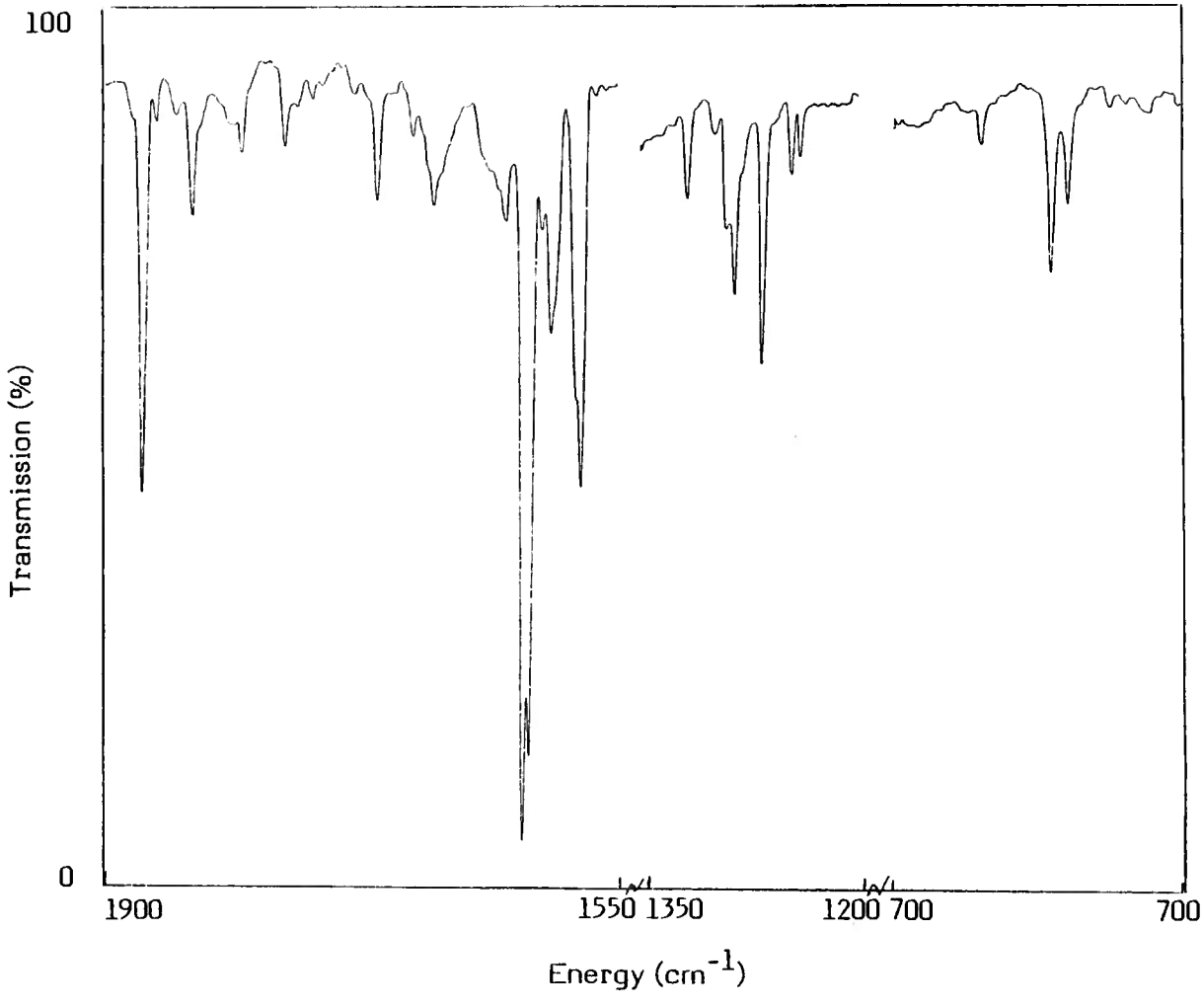


Fig. 1-5. The IR spectra of the gas-phase reaction products of chlorine atoms/argon (1:50) mixtures with $^{15}NO_2$/Ar (1:200) mixtures.

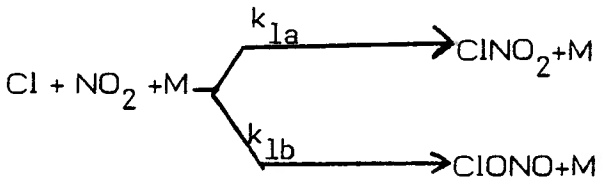
The ratio of k_{1a} to k_{1b} is calculated to be 1:4 using argon as a buffer gas. This suggests that the products ratio should be in the same proportion. The calculated rate constants are dependent on the thermochemical data used. The uncertainty in the k values resulting from the uncertainty in entropy is very significant.[10,11] Niki et al have observed the product ratio of $ClNO_2$ to ClONO as approximately 1:4 by in situ monitoring of the Cl + NO_2 + (M) reaction.[10]

Thermochemical data (Table 1-3) gives ΔG^o for $ClNO_2$ as -24.1 kcal/mole and ΔG^o for ClONO as -14.7 kcal/mole, indicating that $ClNO_2$ is the more stable isomer. The kinetic rate data (p. 23) however indicates that ClONO is produced faster than $ClNO_2$.

In this work, the plot of integrated intensities of $ClNO_2$ (1695.7 cm^{-1}) and ClONO (1719.4 cm^{-1}) vs. reaction pathlength (Fig. 1-6) as well as the integrated intensities (Table 1-4) indicate that both $ClNO_2$ and ClONO are each produced in almost the same amounts. The reaction path is the distance from the sample holder to the inlet of Cl_2/Ar mixture. The integrated intensities of the peaks were determined by weighing. The average of three separate weighings were taken and averaged. The weighings were calibrated using the weight of 1 sq. in. of the same type of paper as standard.

Two separate experiments run under the same experimental conditions were chosen to investigate the reproducibility of $ClNO_2$ and ClONO peaks. Two $ClNO_2$ peaks (1268 and 787 cm^{-1}) and two ClONO peaks (1719 and 837 cm^{-1}) were chosen from each experiment, and the ratio of the $ClNO_2$ peaks and ClONO peaks were

Table 1-3. Thermochemical Data for Chlorine Nitrite (ClONO) and Nitryl Chloride ($ClNO_2$) at 298.15K.[a,b]



	ΔH^o kcal/mol	ΔG^o kcal/mol	ΔS^o (e.u.)
$ClNO_2$ (1a)	-33.6	-24.1	-31.8
ClONO (1b)	-22.6	-14.7	-26.5

a. JANAF Thermochemical Tables, NBSRDS - NBS 37, Washington, D. C., 1970.
b. B. Janowski, Ph.D. Thesis, Kiel University, West Germany, 1975.

Table 1-4. Integrated Intensities of the Products of the Gas-Phase Reaction of Cl + NO_2 (+M).

REACTION PATHLENGTH (cms)	$ClNO_2$[a,b]	ClONO[a,c]	ClNO[a,d]
3.0	0.071	0.009	0.016
12.0	0.063	0.020	0.079
20.0	0.063	0.048	0.092
27.0	0.046	0.019	0.85
35.0	0.070	0.036	0.065

a. Integrated Intensities.
b. The uncertainity in weighing is 1.67%.
c. The uncertainity in weighing is 4.28%.
d. The uncertainity in weighing is 3.05%.

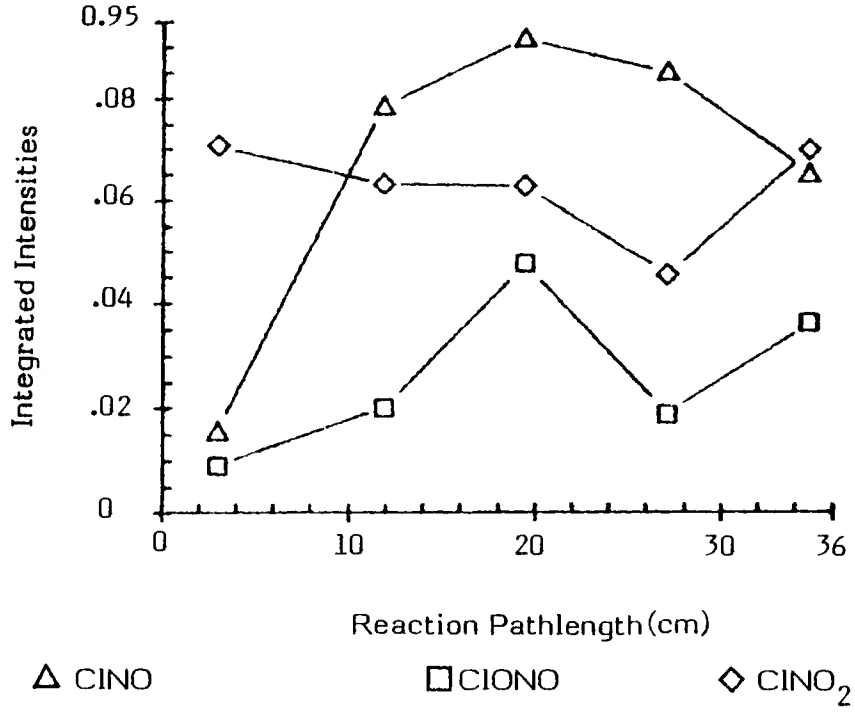


Fig. 1-6. A plot of integrated intensities of $ClNO_2$ (1696 cm^{-1}), ClNO (1782 cm^{-1}), and ClONO (1719 cm^{-1}) against reaction pathlength.

calculated for each experiment (Table 1-5). In the first experiment the ratio of $ClNO_2$ peaks is 3.58 while the ratio in the second experiment is 3.25, so also the ratio of ClONO peaks in the first experiment is 1.02 while the ratio in the second experiment is 1.29. Comparison of the ratios of $ClNO_2$ peaks from the two experiments as well as comparison of the ClONO peaks indicate that $ClNO_2$ and ClONO absorptions are reproducible since the uncertainities in the ratios are within experimental errors not large. For the $ClNO_2$ ratio the uncertainity is ~ 23% while the uncertainity in the ClONO ratio is ~ 10%.

Table 1-5. Integrated Intensity Ratios of $ClNO_2$ Absorptions (1268 and 787 cm^{-1}) and ClONO Absorptions (1719 and 837 cm^{-1}) from Two Separate Experiments but Under the Same Experimental Conditions.

EXPERIMENT	A_1/A_2 [a]	B_1/B_2 [a]
1	3.58	1.02
2	3.25	1.29

a. A_1 is integrated intensity of $ClNO_2$ at 1268 cm^{-1}.
A_2 is integrated intensity of $ClNO_2$ at 787 cm^{-1}.
B_1 is integrated intensity of ClONO at 1719 cm^{-1}.
B_2 is integrated intensity of ClONO at 837 cm^{-1}.

CONCLUSION

The observations indicate that the gas-phase reactions of chlorine atoms with NO_2 proceed along two different channels: the addition of chlorine atoms to the nitrogen atoms of NO_2 to produce the well known nitryl chloride molecule $ClNO_2$[12], and the addition of the chlorine atoms to the oxygen atoms of NO_2 to form ClONO, the chlorine analog of FONO, and HONO.[8,22] The reaction pathlength studies indicate that both $ClNO_2$ and ClONO are each produced within experimental error in almost equal amounts. Niki et al put an upper limit of 20% for the $ClNO_2$ yield and a lower limit of 80% for the ClONO yield using the Fourier Transform Infrared Spectroscopic (FTIR) method.[10] They were able to obtain the above limits because they monitored the concentration of the products in situ using very sensitive instruments. In our studies, the products of the gas-phase reaction travel through a maximum distance of 35.0 cm before they are deposited on the cold CsI window and the infrared spectrum recorded.

The atmospheric implication that can be drawn from this work is that if the dominant removal process of ClONO and $ClNO_2$ is photolysis, and the primary products of their photolysis are the same, i.e. Cl + NO_2, then the presence of two reaction pathways does not influence the ozone budget.[23] If, on the other hand, the two photolyse to yield different primary products, i.e.

$$ClNO_2 \xrightarrow{h\nu} Cl + NO_2 \qquad (1\text{-}9)$$

$$ClONO \xrightarrow{h\nu} ClO + NO \qquad (1\text{-}10)$$

then some effects may be expected, since chlorine atom from (1-9) can go into the following catalytic cycle:

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (1\text{-}11)$$

$$ClO + O \longrightarrow Cl + O_2 \qquad (1\text{-}12)$$

$$O_3 + O \longrightarrow 2O_2 \text{ (net)}$$

or recombine with NO_2 to form $ClNO_2$. The photolysis products from (1-10) however will generate two catalytic cycles

$$ClO + O \longrightarrow Cl + O_2 \qquad (1\text{-}12)$$

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (1\text{-}11)$$

$$O_3 + O \longrightarrow 2O_2 \text{ (net)}$$

and

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad (1\text{-}13)$$

$$NO_2 + O \longrightarrow NO + O_2 \qquad (1\text{-}14)$$

$$O_3 + O \longrightarrow 2O_2 \text{ (net)}$$

It is also possible for ClO to recombine with NO to form ClONO.

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CHAPTER II

LOW TEMPERATURE INFRARED SPECTRA OF CHLORINE NITRATE AND EVIDENCE FOR THE EXISTENCE OF CHLORINE PEROXYNITRATE (CLOONO)

LIST OF FIGURES

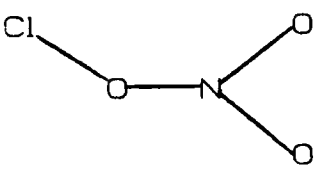
LIST OF TABLES

INTRODUCTION

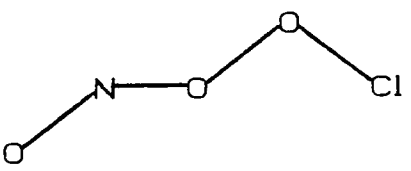
The possible role of chlorine nitrate in stratospheric ozone chemistry was first pointed out by Rowland et al.[1] These authors suggested that $ClONO_2$ may act to lower the net ozone depletion by the ClO_x catalytic cycle by providing a sink for the ClO molecule via the reaction:

$$ClO + NO_2 (+M) \longrightarrow ClONO_2 (+M) \qquad (2\text{-}1)$$

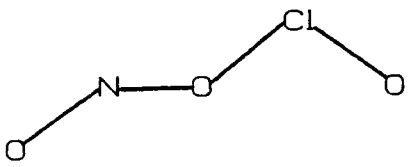
Consequently, the photolysis products and photochemical lifetime of $ClONO_2$ have generated considerable interest, since they would play a vital role in the ultimate impact of $ClONO_2$ on the ClO_x ozone depletion cycle. However, Smith et al and Chang et al obtained conflicting experimental evidence for the photolysis products.[2,3] The former measured ClONO + O and the latter, using the very low pressure pyrolysis (VLPP) technique, measured Cl + NO_3 as the products of $ClNO_3$ decomposition. These results led Molina et al to propose four isomers for $ClONO_2$:[4]



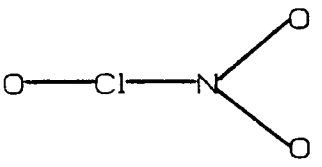
(A)



(B)



(C)



(D)

Molina et al also proposed that a short photochemical lifetime for $ClONO_2$ decreases its importance as a sink for ClO.[4] Although the previously mentioned authors have studied this system intensely using two techniques; Fourier Transform Infrared Spectroscopy, and Flash Photolysis - Ultraviolet Absorption, no direct evidence exists for the presence of one or more isomers.

In this study, the technique of matrix-isolation is employed, in conjunction with infrared spectroscopy, to isolate $ClONO_2$, and identification of the isomers is attempted using the resulting infrared spectra. The experiments involve taking the low temperature infrared spectra of synthetic chlorine nitrate at various dilution ratios.

EXPERIMENTAL

The experimental techniques employed in these experiments have been previously described in Chapter I. The apparatus (an Air Products cryotip and displex refrigerator) and the high vacuum manifold have also been described. Clean-up procedures are also identical to those described in Chapter I. Purification of Cl_2 and NO_2 was also carried out as described in the last chapter.

The synthetic chlorine nitrate was prepared following the procedure of Schmeisser.[5] Purified Cl_2O and N_2O_5 were reacted in the liquid state under an atmosphere of ozonized oxygen. The crude product was purified by trap to trap distillation using an ethyl bromide and liquid nitrogen slush. Chlorine was removed by pumping at 154K. Repetitive distillation at 195K removed NO_2. The purified chlorine nitrate was stored at 77K and used as desired. The infrared spectra of the purified chlorine nitrate still showed traces of nitrogen dioxide.

Mixtures of chlorine nitrate and argon (Matheson, U. H. P.) were made using standard manomeric techniques. Chlorine nitrate and argon mixtures ranging from (1:100) to (1:1500) were deposited on the CsI window held at 10K by the Air Products Cryotip and helium refrigerator (Model CSA-200) described before (Chapter I). The deposition of mixtures ranging from (1:100) to (1:1500) makes it possible to note the differences between mixtures of high dilution and those of low dilution. In each dilution, argon forms an intracage in which molecular and reactive species are trapped. The more the dilution, the larger the cage formed by argon in the matrix.

This separates out the different species as far from each other as possible. The infrared spectrum of such a mixture will show absorptions due to individual species present. The peaks are sharp and well resolved as the distances provided by the argon cages prevent intermolecular reaction and eliminate dipole-dipole interaction. Also reaction between reactive species is reduced if not eliminated. Fig. 2-1 shows the spectrum of (1:100) mixture, in which the peaks are not sharp and well resolved. Fig. 2-2, however, shows the spectrum of (1:1500) mixture, in which the peaks are sharp and well resolved. The temperature was controlled by a resistance heater mounted on the cold tip and measured by an Air Products APDIC-2 thermocouple. The typical deposition rate was 2.0-2.5 mmoles/hr and the amount deposited ranged from 3-5 mmoles.

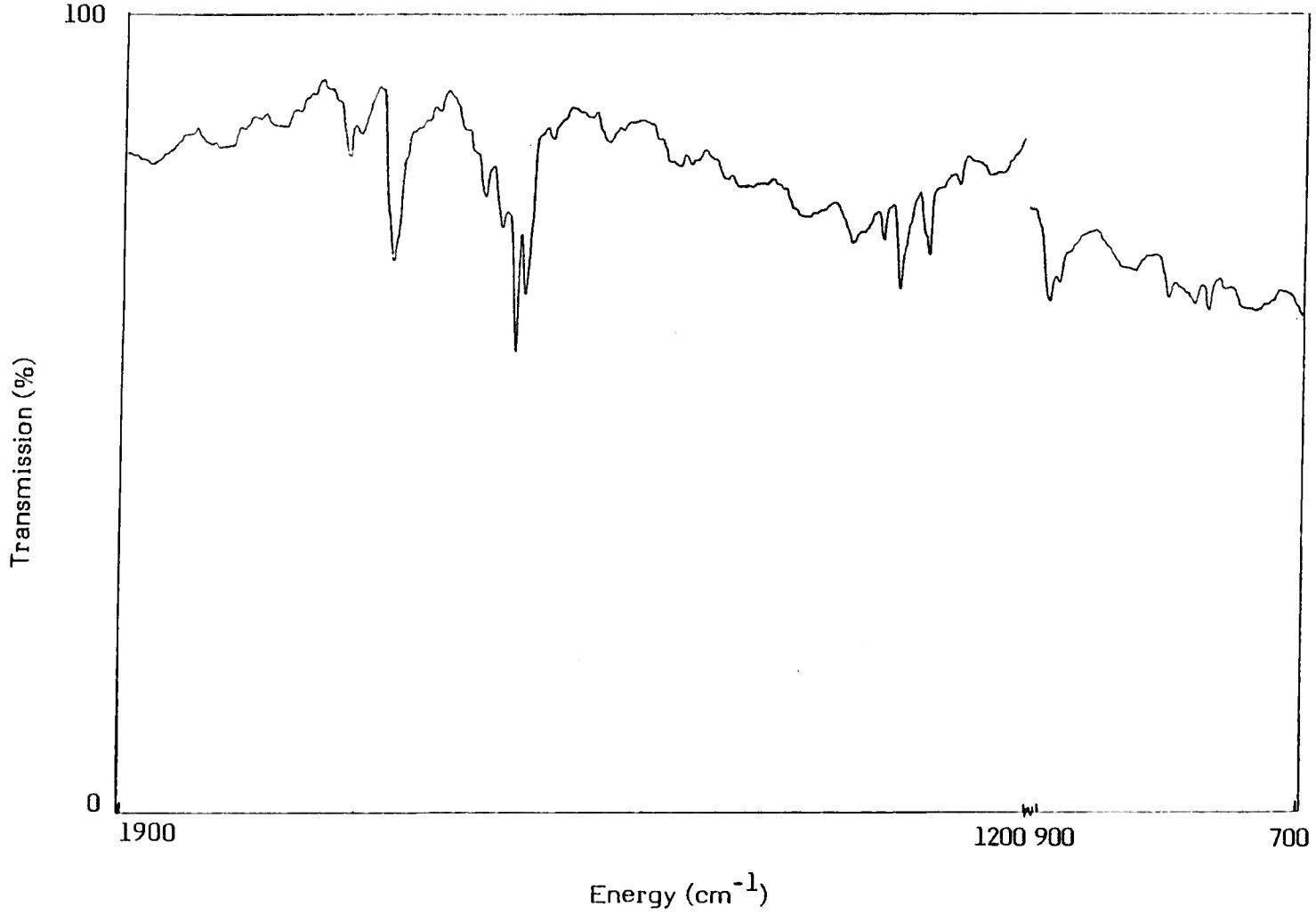


Fig. 2-1. Infrared spectrum of synthesized $ClNO_3$/Ar (1:100) in the 1900 - 700 cm^{-1} spectral region.

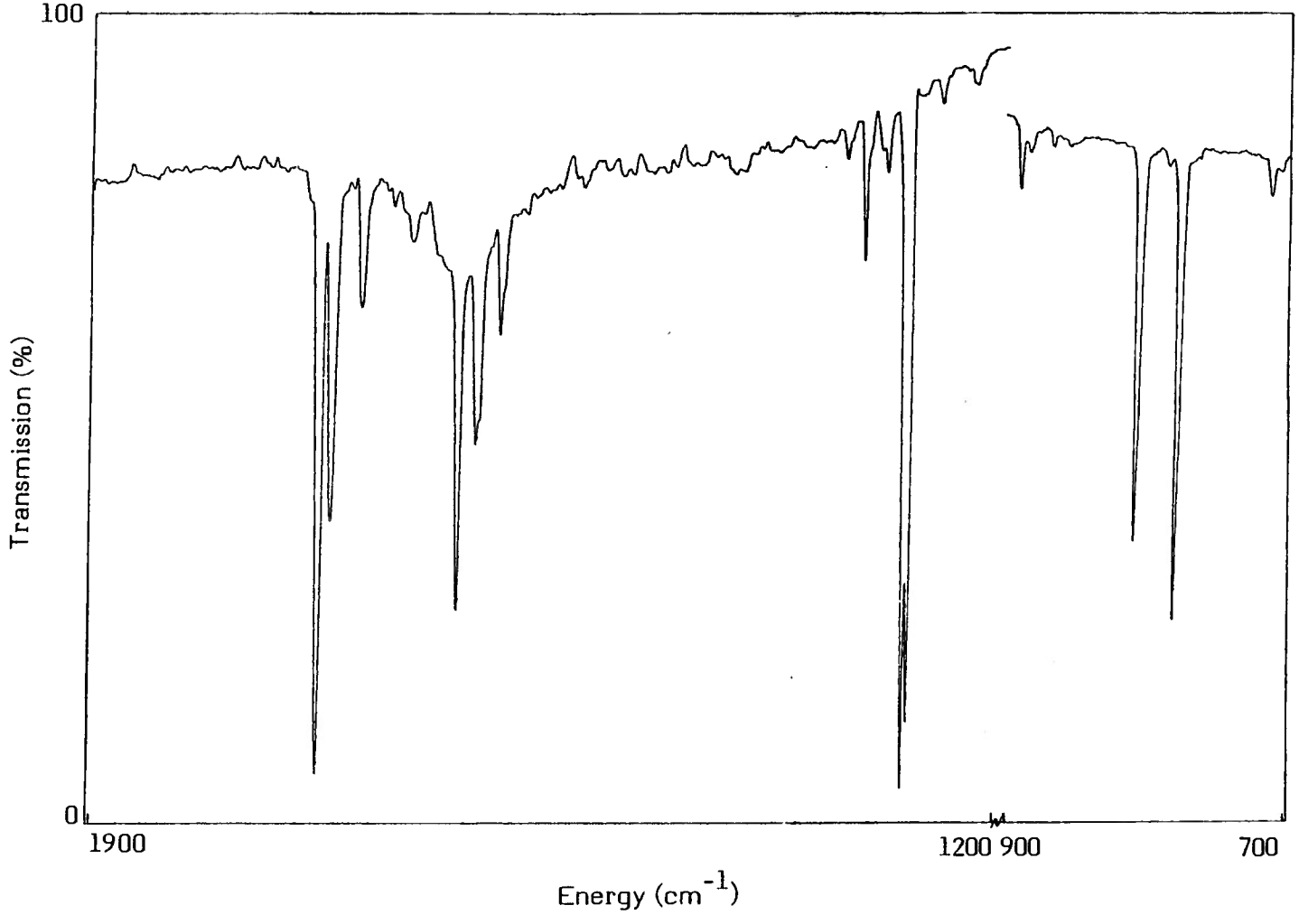


Fig. 2-2. Infrared spectrum of synthesized $ClNO_3$/Ar (1:1500) in the 1900 - 700 cm^{-1} spectral region.

RESULTS AND DISCUSSION

The matrix isolated infrared spectrum of the bulk synthesized $ClONO_2$ is given in Fig. 2-3. On warming the sample to 30K, the absorptions labelled A ($ClONO_2$) increased in intensity, while those labelled B (ClOONO) decreased in intensity, indicating the presence of at least two differently behaving species. When the sample was warmed to 40K and then recooled to 10K, the spectra exhibited the features of solid chlorine nitrate ($ClONO_2$), in agreement with the IR spectrum of solid $ClONO_2$ of Miller et al.[6]

Moreover, calculations of the integrated intensity ratios of A absorptions (1730 and 1303 cm^{-1}) and B absorptions (1718 and 1333 cm^{-1}) were carried out before and after warming, and the results (Table 2-1) show that the ratio of the A absorption (1730 and 1303 cm^{-1}) before warming is 8.1 and after warming it is 7.6, while the ratio of the B absorptions (1718 and 1333 cm^{-1}) before warming is 10.5 and after warming is 11.4. Comparison of the A absorptions ratios before and after warming indicate that A peaks behave as a group. Comparison of the B absorptions ratios before and after warming also indicate that B peaks behave as a group.

Considering the isomers A through D (page 38), each will have at least one characteristic absorption not shared by the other three. For example, structure B will exhibit absorptions due to O-O stretch and O-O-Cl bend, while structure C will have an absorption arising from the O-Cl-O bend and structure D

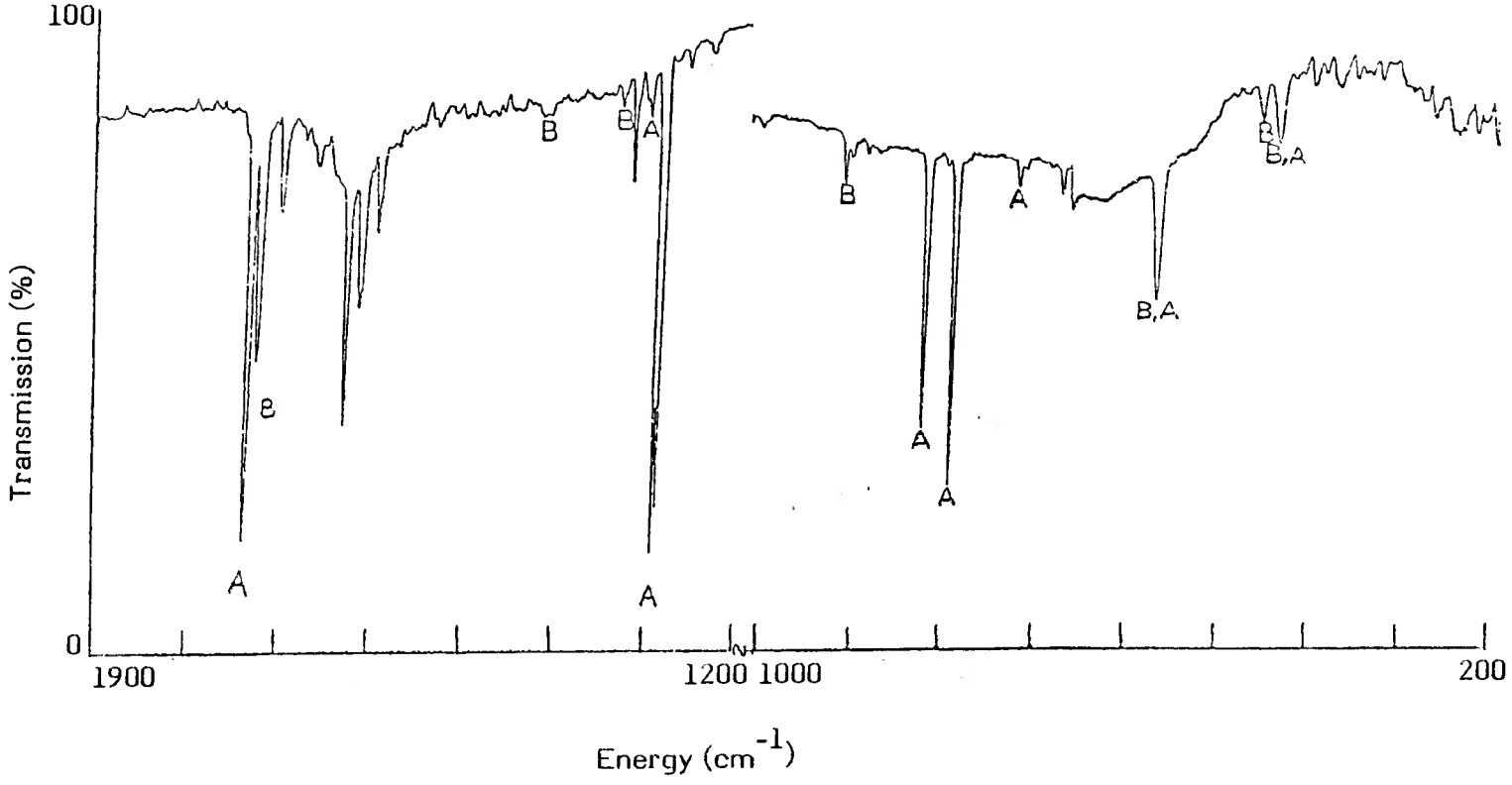


Fig. 2-3. Infrared spectrum of synthesized chlorine nitrate. (A) represent absorptions due to $ClONO_2$; and (B) represent absorptions due to ClOONO.

Table 2-1. Table Showing the Integrated Intensity Ratios of $ClONO_2$ Absorptions (1730 and 1303 cm^{-1}) and ClOONO Absorptions (1718 and 1333 cm^{-1}) Before and After Warm-up Studies.

	A_1/A_2 [a]	B_1/B_2 [a]
Before Warming	8.08	10.52
After Warming	7.60	11.4

a. A_1 is integrated intensity of $ClONO_2$ at 1730 cm^{-1}.
A_2 is integrated intensity of $ClONO_2$ at 1303 cm^{-1}.
B_1 is integrated intensity of ClOONO at 1718 cm^{-1}.
B_2 is integrated intensity of ClOONO at 1333 cm^{-1}.

will show an absorption due to N-Cl stretch. The different molecular structures of these isomers coupled with the known absorptions for ClO, ClOO, OClO and O_2NO make it possible to predict which of these isomers may be present in the sample.

Structure C should exhibit the OClO bend (445 cm^{-1}), and ClO asymmetric stretch (945 cm^{-1}). The N=O stretch is in the region 1700 - 1750 cm^{-1} as estimated by the attachment of various functional groups to N=O.[7] Additionally, structure C, as well as A, should show an absorption due to the NOCl bend. This NOCl bend is evident at 1306 cm^{-1}; however, there are no absorptions at or near 945 cm^{-1} and 1100 cm^{-1}, therefore structure C can tentatively be excluded.

Similarly, structure D should exhibit an N-Cl stretch, and based on the Cl-N stretch in ClNO (595.8 cm^{-1}) and $ClNO_2$ (792.6 cm^{-1}), the Cl-N stretch in $OClNO_2$ should be expected to occur in the 550 - 800 cm^{-1} region. At present, it is impossible to correlate the observed frequencies with the expected absorption frequencies of $OClNO_2$.

Isomer B will have vibrational frequencies close to those of ClOO (O-O stretch at 1442 cm^{-1} and Cl-O asymmetric stretch at 430 cm^{-1}.[8] Absorptions at 1431.9 cm^{-1} and 428.2 cm^{-1} were observed, and were attributed to the O-O stretch and Cl-O stretch in ClOONO. This isomer should also show absorptions near those of O_2NO (Table 2-2). In particular, the N=O stretch from O_2NO should be shifted to 1720 - 1750 cm^{-1} region by addition of the heavy chlorine atom. Similar shifts have been observed when FO_2, NO_2 and Cl were added to NO.[9] Thus the assigned absorption

Table 2-2. Vibrational Energy of O_2NO.[a,b]

VIBRATIONAL ENERGY (CM^{-1})	VIBRATIONAL MODE
1845	N=O stretch
955	N=O stretch
1400	O-O stretch
540	ONO bend
454	OON bend

a. W. A. Guillory and H. Johnson, J. Chem. Phys., 42, 2457 (1965).

b. S. C. Bhatia and J. H. Hall, Jr., J. Phys. Chem., 84, 3255 (1980).

at 1717.6 cm^{-1} is attributed to the N=O stretch of isomer B. The absorptions at 1431.9 cm^{-1} and 428.2 cm^{-1} are attributed to the O-O and ClO stretches, respectively, and considering the O_2NO absorptions in Table 2-2, the absorptions at 931.3 cm^{-1}, 556.3 cm^{-1} and 445.6 cm^{-1} are assigned to the N-O stretch, ONO bend, and the OON bend, respectively in ClOONO. These assignments are summarized in Table 2-3.

Chang et al have proposed a set of vibrational frequencies for ClOONO; however, several assignments are inconsistent with the accepted assignments for certain functional groups in ClOONO as well as in $ClONO_2$.[3] These authors assign the 1735 cm^{-1} absorption in both $ClONO_2$ and ClOONO to a ClO stretch. However, the ClO stretch in $ClONO_2$ definitely occurs at 809 cm^{-1} and the 1735 cm^{-1} absorption in ClOONO is more indicative of an N=O stretch. These authors also give the O-O stretch as occuring at 880 cm^{-1}, and do not consider the 1431.9 cm^{-1} absorption assigned (and observed in this work) to be O-O stretch. Again the 1431.9 cm^{-1} absorption is in the expected region based upon the 1442 cm^{-1}, O-O stretch in ClOO. The 858 cm^{-1} stretch was assigned to the N-O stretching mode by these authors; however, considering the observed N-O stretching modes in HNO_3 and O_2NO, this vibrational mode would occur at approximately 931.3 cm^{-1}, consistent with our observations. These authors assign the N=O stretch to the 710 cm^{-1} absorptions. However, reasonable assignments of the 855.1 cm^{-1} and 705.1 cm^{-1} absorptions cannot be made.

Table 2-3. Observed Molecular Vibrational Energy (cm^{-1}) for $ClONO_2$ and ClOONO in Synthesized Chlorine Nitrate/Argon (1:1000).

$ClONO_2$		ClOONO	
Energy (cm^{-1})	Vibrational Mode	Energy (cm^{-1})	Vibrational Mode
1726.9	NO_2 asy-stretch	1717.6	N=O stretch
1287.6	NO_2 asy-stretch	1431.9	O-O stretch
807.7	OCl stretch	931.3	N-O stretch
781.3	NO_2 scissoring	855.05	--
556.3	NO stretch	705.1	--
428.2	NO_2 rock	556.3	ONO bend
273.2	OCl bend	445.6	OON bend
		428.2 or 412	ClO stretch

CONCLUSION

The observations indicate that in the low temperature infrared study of matrix-isolated synthetic chlorine nitrate, at least two isomers ($ClONO_2$ and ClOONO) are present in the samples. The other species, OClONO and $OClNO_2$ are absent in the samples. The atmospheric implication of this is that chlorine nitrate is an important sink molecule due to its low absorption coefficient, and if ClOONO has the same or even lower absorption coefficient it will be an important sink molecule, too. However, their primary photolysis products are not the same since $ClONO_2$ photolyse to give Cl + NO_3 and/or ClONO + O.[2,10]

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CHAPTER III

MATRIX-ISOLATED INFRARED SPECTROSCOPIC STUDIES OF THE GAS-PHASE REACTIONS OF: (a) Cl + Cl_2O + NO_2 (+M); (b) Cl + O_3 + NO_2 (+M)

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

The possibility of producing chlorine nitrates from gas-phase reactions is investigated. In the reaction of chlorine atoms with Cl_2O, the following reaction takes place:

$$Cl_2O + Cl \longrightarrow ClO + Cl_2 \qquad (3\text{-}1)$$

The ClO molecules can then react with NO_2 to give chlorine nitrates.

The reaction of chlorine atoms with ozone has been studied in detail and the workers claim that when Cl_2/Ar mixture is subjected to a microwave discharge and the chlorine atoms produced are reacted with O_3, the primary products formed are OClO (1105 cm^{-1} and 940 cm^{-1}) and ClOO (1442 cm^{-1}).[1,2] These absorptions were also observed by Arkell and Schwager.[3] If OClO and ClOO are reacted with NO_2, some uncharacterized products (3-2) - (3-5) might be formed. The rate constants for

$$OClO + NO_2\ (+M) \longrightarrow OClOONO \qquad (3\text{-}2)$$

$$OClO + NO_2\ (+M) \longrightarrow OClONO_2 \qquad (3\text{-}3)$$

$$ClOO + NO_2\ (+M) \longrightarrow ClOONO_2 \qquad (3\text{-}4)$$

$$ClOO + NO_2\ (+M) \longrightarrow ClOOONO \qquad (3\text{-}5)$$

these reactions are not yet known. However if ClO is also produced or is the primary product of Cl + O_3 and/or Cl + Cl_2O reactions, then the reaction (3-6) is also expected.

$$ClO + NO_2 \longrightarrow \text{chlorine nitrates} \qquad (3\text{-}6)$$

In this work the gas-phase reaction of chlorine atoms with O_3 and NO_2 as well as the gas-phase reaction of chlorine atoms with Cl_2O and NO_2 is investigated. The products of the reactions are analyzed using low temperature matrix infrared spectroscopy.

EXPERIMENTAL

The chlorine and NO_2 used in these sets of experiments were carefully purified as described in Chapter I of this thesis.

Chlorine monoxide was prepared following the procedure of Schack and Lindahl[4] by allowing 0.69 moles of chlorine at 0.73 atm to react with 21.7g of yellow HgO in a 2-liter bulb kept in a N_2/trichloroethylene bath (-73^{o}) for 5 days. The crude product was trap to trap distilled to remove volatile materials, and high yields of purified Cl_2O was obtained. The stoichiometry of the reaction approaches

$$2Cl_2 + HgO \longrightarrow Cl_2O + HgCl_2 \qquad (3\text{-}7)$$

Identity and purity of the product was verified by infrared analysis. Cl_2O absorbs at 675 cm^{-1} and 635 cm^{-1}. The purified Cl_2O was stored at 77 K and only the required amount was pumped out of the cooled reactor.

Caution: Since chlorine monoxide is very sensitive to heat and shock and may explode, safety shields were used and goggles and gloves were worn when handling it. Contact of chlorine monoxide and N_2O_5 with organic matter was excluded, and moisture was carefully avoided. Perfluorinated hydrocarbons, e.g., fluorolube, was used for joint lubrication.

The typical mixtures used for the gas-phase production of chlorine nitrate were Cl_2O/Ar (1:10), Cl_2/Ar (1:50), and NO_2/Ar (1:200). In all of the experiments Cl_2O/Ar was introduced from inlet 1 of the quartz kinetic cell (Fig. 1-2) shown in Chapter I of this thesis, the points of introduction of Cl_2/Ar and NO_2/Ar were varied starting with Cl_2/Ar in inlet 2 and NO_2/Ar in inlet 3. This varied the reaction pathlength from 35 - 12.5 cm. In a typical experiment 2.3×10^{-4} mmoles of chlorine atoms was allowed to react with 7.9×10^{-4} mmoles of Cl_2O and 1.3×10^{-4} mmoles of NO_2. Deposition time ranged from 1.7 - 2.1 hrs. The products of the gas-phase reaction in the kinetic cell were matrix-isolated on the cold CsI window.

The purified Cl_2O was reacted with:

(1) argon discharge,

(2) nitrogen dioxide, and

(3) chlorine atoms,

to see if any products would be formed. In the first experiment Cl_2O/Ar (1:50) and pure argon discharge were co-deposited on the cold CsI window. The infrared spectrum showed peaks due to Cl_2O, CO_2, matrix-isolated water, and NO formed from argon discharge. The nitrogen of the NO is from N_2 which is an impurity in argon. A total of three experiments were carried out for the reaction of Cl_2O/Ar (1:50) with NO_2/Ar (1:200), and in all the experiments, infrared spectra indicate peaks due to the Cl_2O, NO_2, CO_2 and matrix-isolated water. In the third set of experiments, gas mixtures ranging from (1:10) to (1:50) were used, and the best yield of ClO was obtained using Cl_2O/Ar (1:10) and Cl_2/Ar (1:50) (Fig. 3-1).

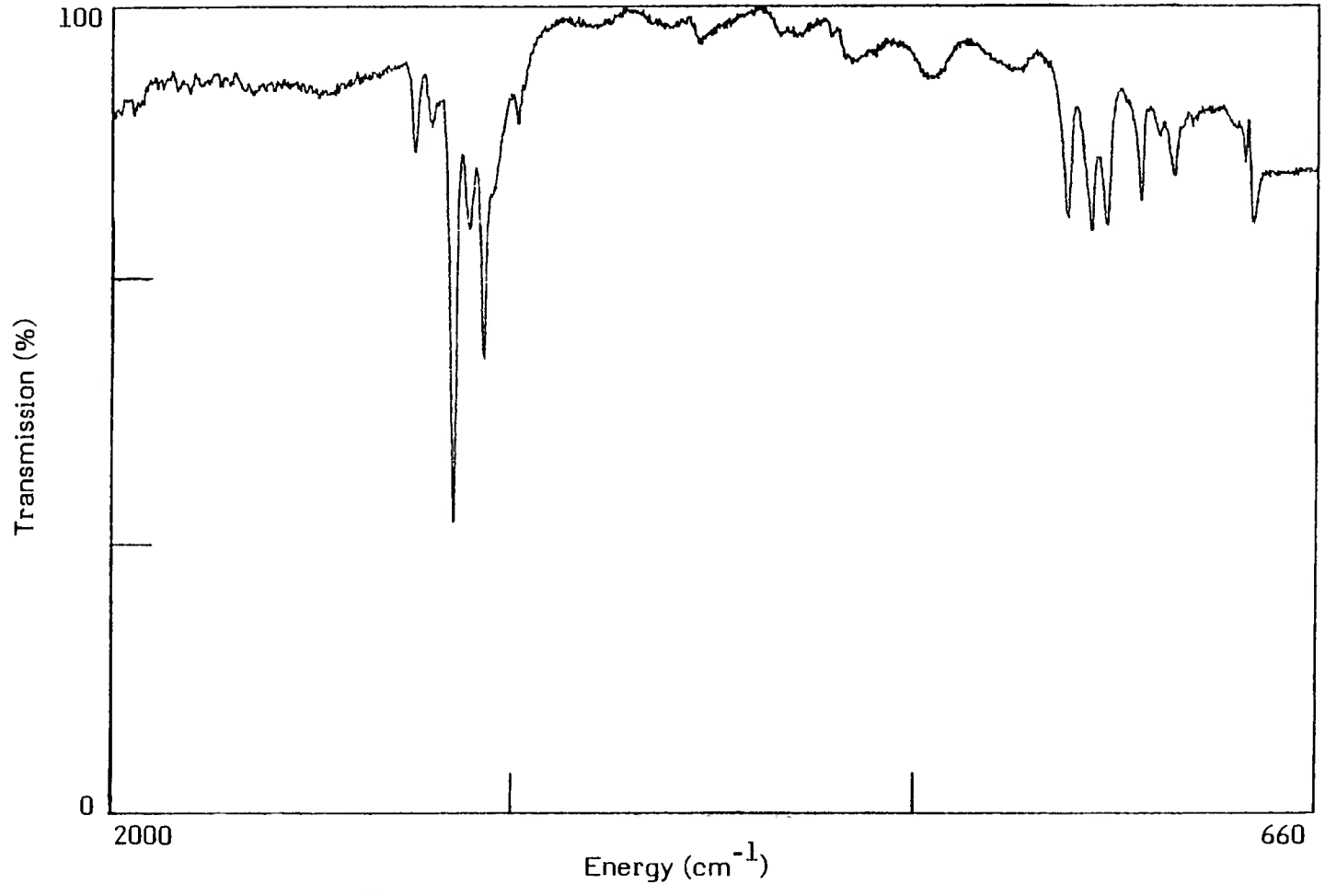


Fig. 3-1. The IR spectra of the gas-phase reaction products of chlorine atoms/argon (1:50) with Cl_2O/Ar (1:100).

A detailed study of the gas-phase reaction of chlorine atoms with NO_2 was also carried out. This provided evidence for the products of the possible side reactions of chlorine atoms with NO_2. (Chapter I)

Ozone was prepared by a "static method" whereby oxygen at pressures less than 0.1 atm was discharged; using a Tesla coil, through a Pt wire, vacuum sealed into a 12 X 0.5 in. Pyrex tube. The lower part of the tube, immersed in liquid nitrogen, was filled with molecular sieve to stabilize the liquid ozone. The ozone condensed as a blue-purple liquid. The trapped ozone was subsequently pumped on for 0.5 hr to remove residual oxygen and volatile impurities. The infrared spectra showed absorption attributable only to ozone. The $^{18}O_3$ used for isotopic studies was prepared from $^{18}O_2$, but at pressures less than 0.08 atm.

Gas mixtures were prepared by standard manometric techniques. Chlorine atoms are produced as described in Chapter I and possible side reactions of Ar* (excited argon) were investigated (Chapter I).[1] In the set of experiments involving $Cl + O_3 + NO_2$ (+M) reactions, pure O_3, Cl_2/Ar (1:25), and NO_2/Ar (1:200) mixtures were used; and 7.65×10^{-4} mmoles of chlorine atoms were allowed to react with 231.2×10^{-4} mmoles of ozone and 1.56×10^{-4} mmoles of NO_2. Deposition time ranged from 1.67 - 1.74 hrs.

RESULTS AND DISCUSSION

The low temperature infrared spectra of the gas-phase reaction products of Cl + Cl_2O + NO_2 (+M) show absorptions in the 1700 - 1740 cm^{-1} region (Fig. 3-2). Expanded spectra of this region has four peaks occuring at 1736 cm^{-1} (a shoulder) 1727 cm^{-1}, and a doublet at 1719 cm^{-1} and 1714 cm^{-1} (Table 3-1). The absorption at 1727 cm^{-1} is close to the observed 1726.9 cm^{-1} in our matrix-isolated spectra of $ClONO_2$. Thus we assign this peak to the N=O stretch of $ClONO_2$. The presence of $ClONO_2$ is further confirmed by the appearance of absorption peaks at 1286.3 cm^{-1} (NO_2 asy-stretch), 817.6 cm^{-1} (ClO stretch), 784.4 cm^{-1} (NO_2 scis), and 558.2 cm^{-1} (NO stretch). These absorption peaks are also observed in the matrix-isolated spectra of synthesized chlorine nitrate (Table 2-3, Chapter II). The presence of the doublet 1710 - 1720 cm^{-1} is an indication that two molecular species are present. This observation is further confirmed by the absence of a doublet in the bulk sample (Fig. 2-3, Chapter II), as well as in the low temperature infrared study of the gas-phase reaction of Cl + NO_2 (+M) (Chapter I). The ClONO, which is a product in the reaction of chlorine atoms with nitrogen dioxide has a strong infrared absorption at 1715 cm^{-1}, and the same vibrational peak has been observed at 1719 cm^{-1}.[5] The chlorine peroxynitrate also has an absorption at 1717.6 cm^{-1} (Table 2-3, Chapter II). Thus it is difficult to assign the individual peaks (1719 and 1714 cm^{-1}) to a particular molecular species, but it is certain that both ClOONO and ClONO are present and give rise to a doublet in the 1700 - 1720 cm^{-1} region. Other peaks which are assigned to ClOONO, from the bulk - synthesized compound (Table 2-3, Chapter II)

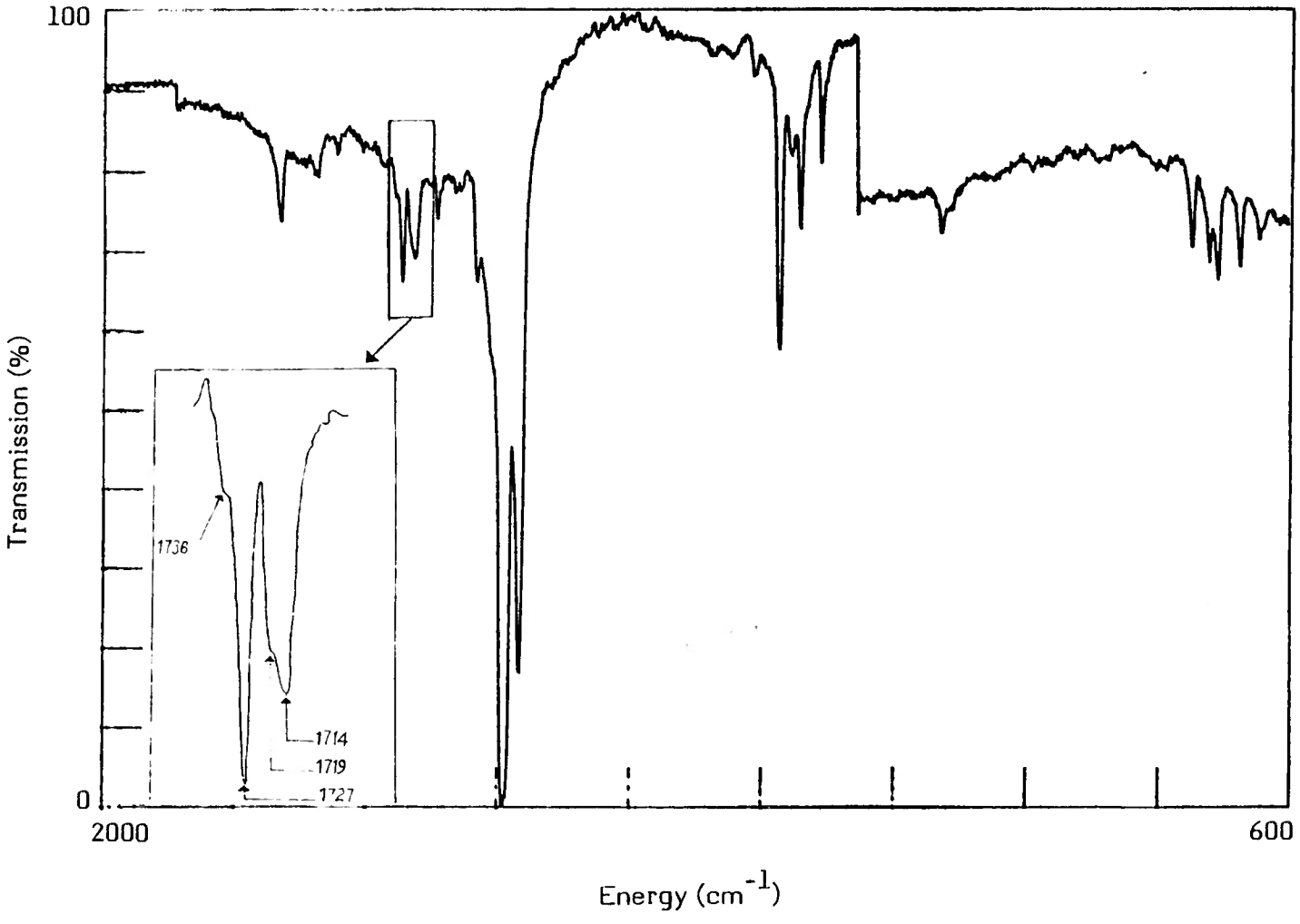


Fig. 3-2. The IR spectra of the gas-phase reaction products of chlorine atoms with Cl_2O and NO_2, reaction pathlength 3 cm.

Table 3-1. Observed Molecular Vibrational Energy (cm^{-1}) for $ClONO_2$ and ClOONO Produced in the Gas-phase Reaction Cl + Cl_2O + NO_2 (+M).

$ClONO_2$		ClOONO	
Energy (cm^{-1})	Vibrational Mode	Energy (cm^{-1})	Vibrational Mode
1726.9	NO_2 asy-stretch	1735.7	N=O stretch
1286.3	NO_2 asy-stretch	1719.4	N=O stretch
808.8	OCl stretch	1417.6	O-O stretch
784.4	NO_2 scissoring	923.8	N-O stretch
558.2	NO stretch	848.8	--
423.8	NO_2 rock	558.2	ONO bend
270.1	OCl bend	448.8	OON bend
		433.2 or 414.4	ClO stretch

are too weak to be observed in our infrared spectra. Figs. 3-2 through 3-6 show the effect produced by variation in reaction pathlength.

Thermochemical data (Table 3-2) gives ΔG^{o} for $ClONO_2$ as -14 kcal/mole and ΔG^{o} for ClOONO as -9.9 kcal/mole, indicating that $ClONO_2$ is the more stable isomer. The kinetic rate data (p. 70) however indicates that ClOONO is produced faster than $ClONO_2$.

In this work comparison of the integrated intensities (Table 3-3) as well as the plot of integrated intensities of $ClONO_2$ (1727 cm^{-1}) and ClOONO (1719 or 1714 cm^{-1}) vs. reaction pathlength (Fig. 3-7) indicate that both $ClONO_2$ and ClOONO are each produced in almost the same amounts. Hence the relative stabilities of the isomers cannot be determined from this work.

In the gas-phase reaction of chlorine atom/argon (1:25) with pure O_3, absorptions observed are those due to ClO (845 cm^{-1}) and a weak absorption due to OClO (1104 cm^{-1}).[3,6,7] The reaction of NO_2 with pure O_3, however shows absorptions due to nitrogen oxides (Table 3-4).[8]

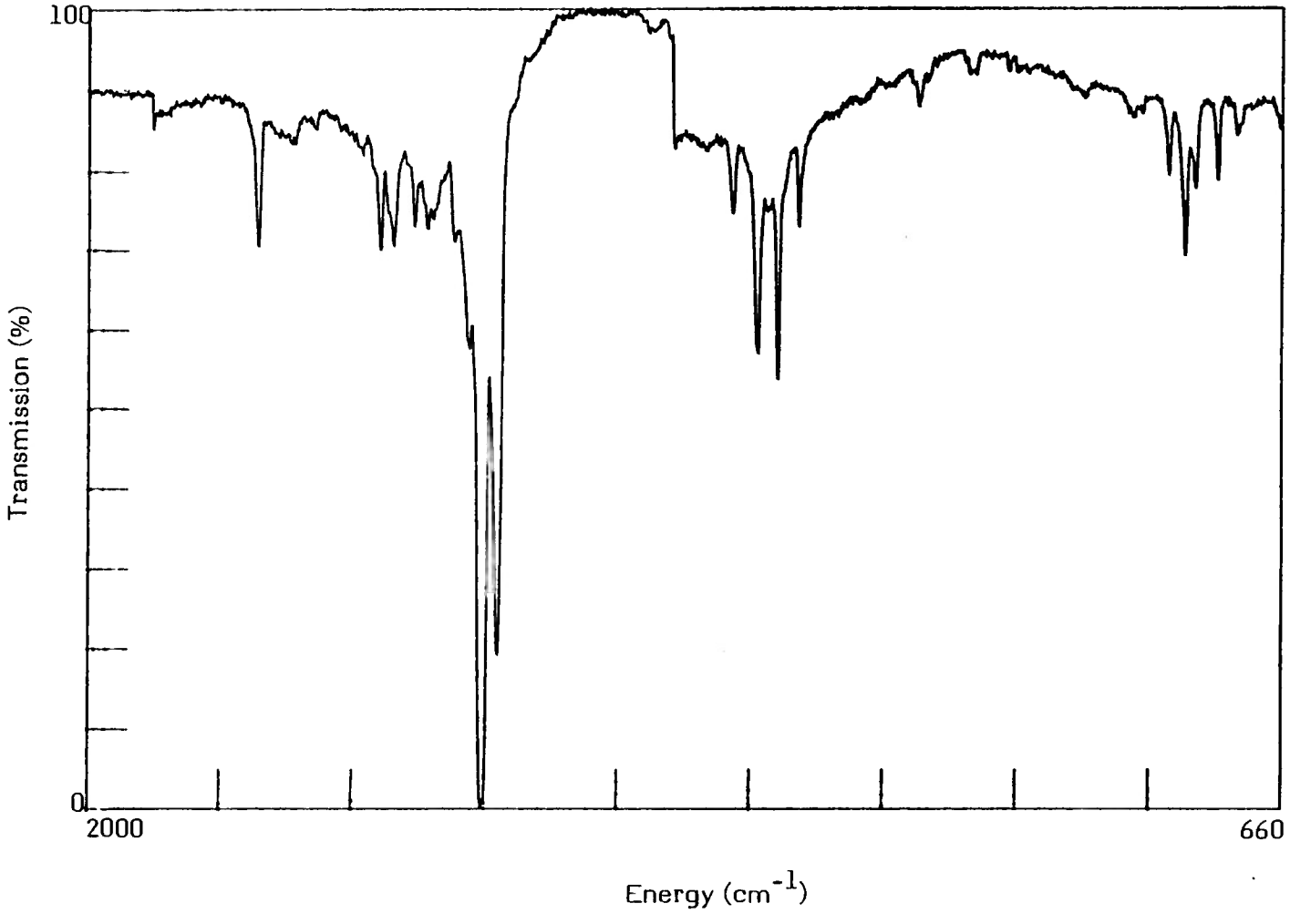


Fig. 3-3. The IR spectra of the gas-phase reaction products of chlorine atoms with Cl_2O and NO_2, reaction pathlength 11.9 cm.

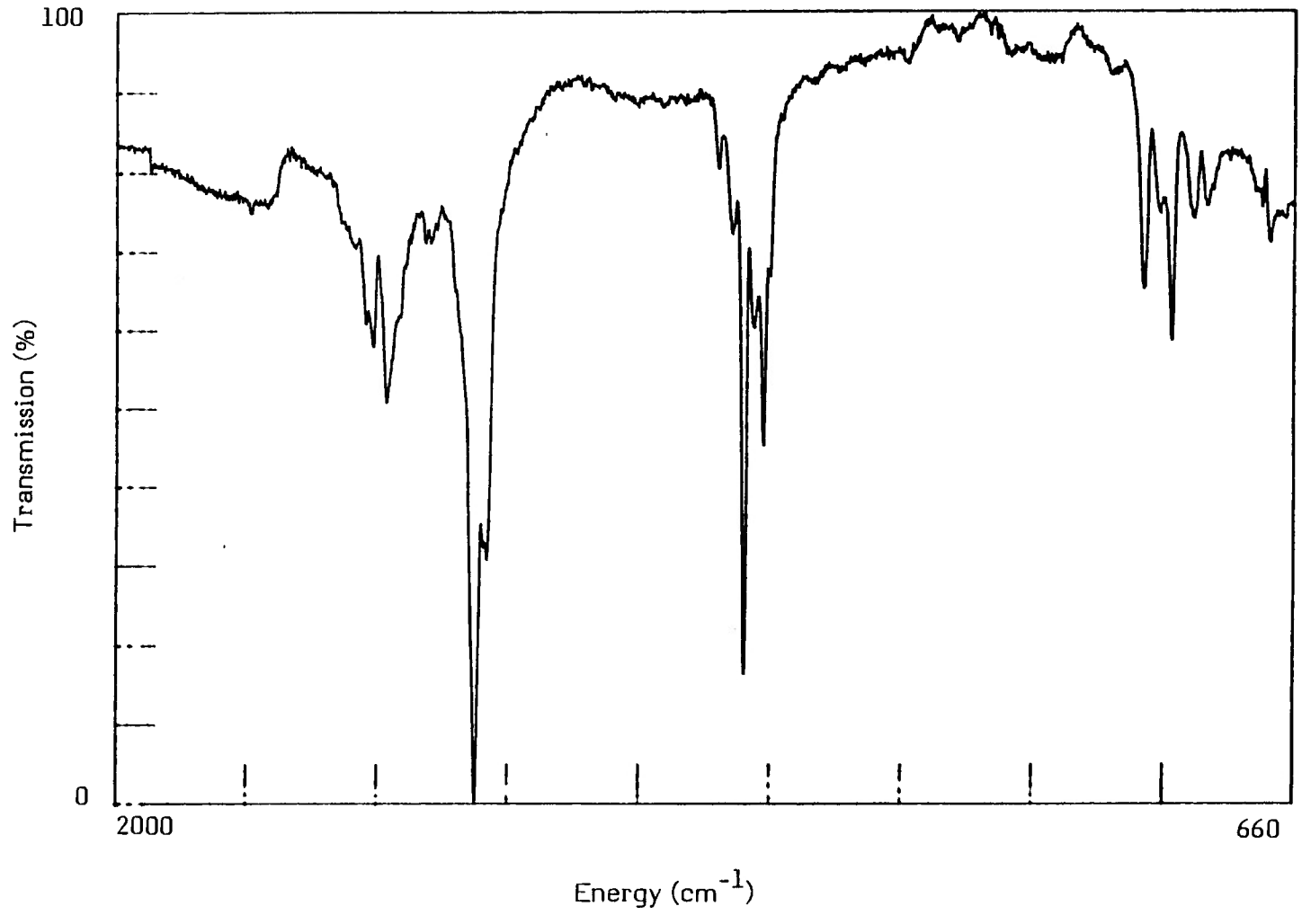


Fig. 3-4. The IR spectra of the gas-phase reaction products of chlorine atoms with Cl_2O and NO_2, reaction pathlength 19.5 cm.

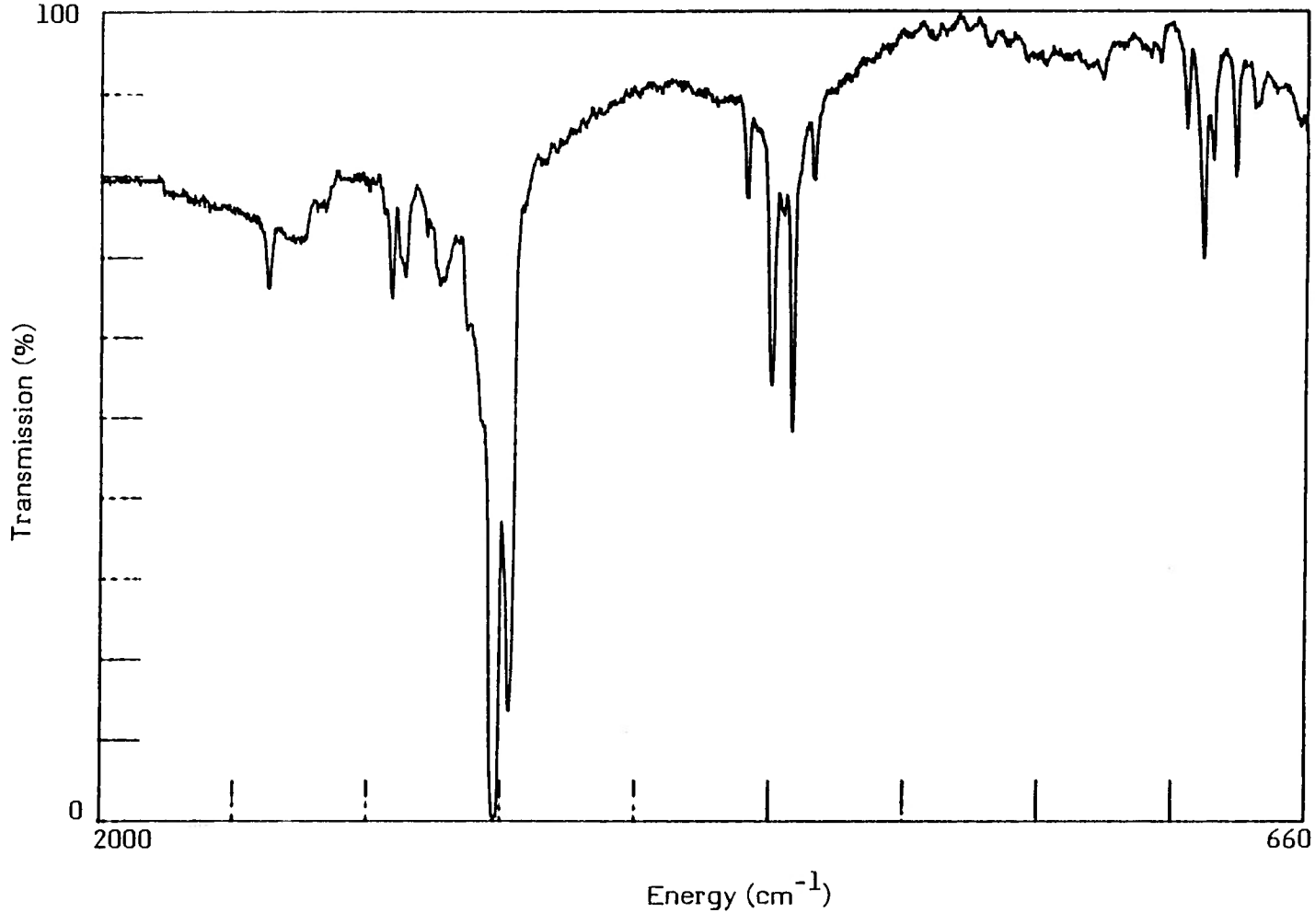


Fig. 3-5. The IR spectra of the gas-phase reaction products of chlorine atoms with Cl_2O and NO_2, reaction pathlength 27.1 cm.

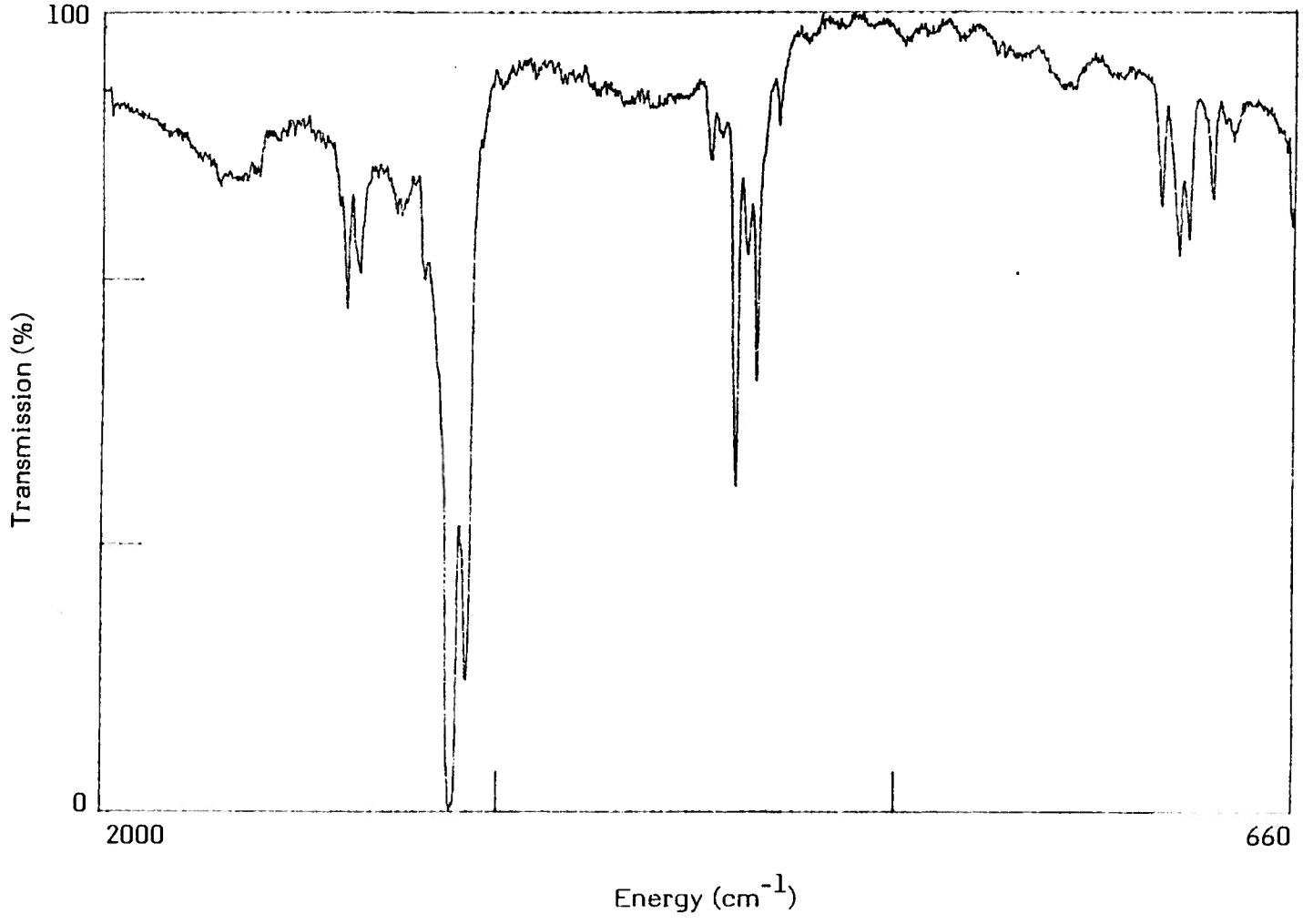
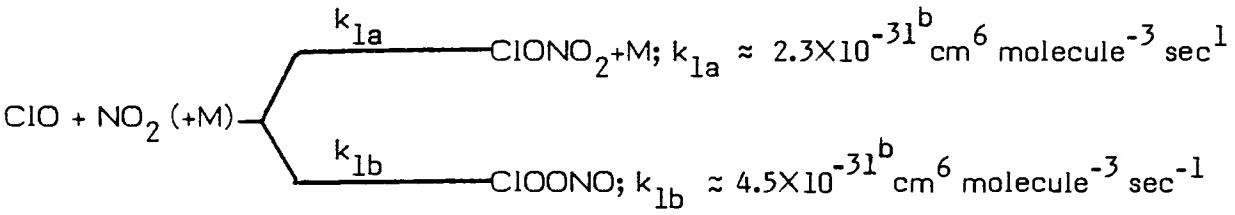


Fig. 3-6. The IR spectra of the gas-phase reaction products of chlorine atoms with Cl_2O and NO_2, reaction pathlength 34.8 cm.

Table 3-2. Thermochemical Data for $ClONO_2$ and ClOONO at 298.15K.[a]



	Δ H^o kcal/mol	Δ G^o kcal/mol	Δ S^o (e.u.)
$ClONO_2$ (1a)	-26.1	-14	-40.6
ClOONO (1b)	-20.6	-9.9	-36.0

a. R. H. Miller, D. L. Bernitt, and I. C. Hisatune, Spectrochin Acta, Part A, 23, 223 (1967).

b. J. S. Chang, A. C. Baldwin, and D. M. Golden, J. Chem. Phys., 71, 2021 (1979).

Table 3-3. Integrated Intensities of the Products of the Gas-Phase Reaction of Cl_2O + Cl + NO_2 (+M).

Reaction Pathlength (cms)	$ClONO_2$[a,b]	ClOONO[a,c]
3.0	0.109	0.107
12.0	0.100	0.083
20.0	0.164	0.122
27.0	0.120	0.119
35.0	0.164	0.103

a. Integrated intensities.

b. The uncertainty in weighing is 2.6%.

c. The uncertainty in weighing is 6.4%.

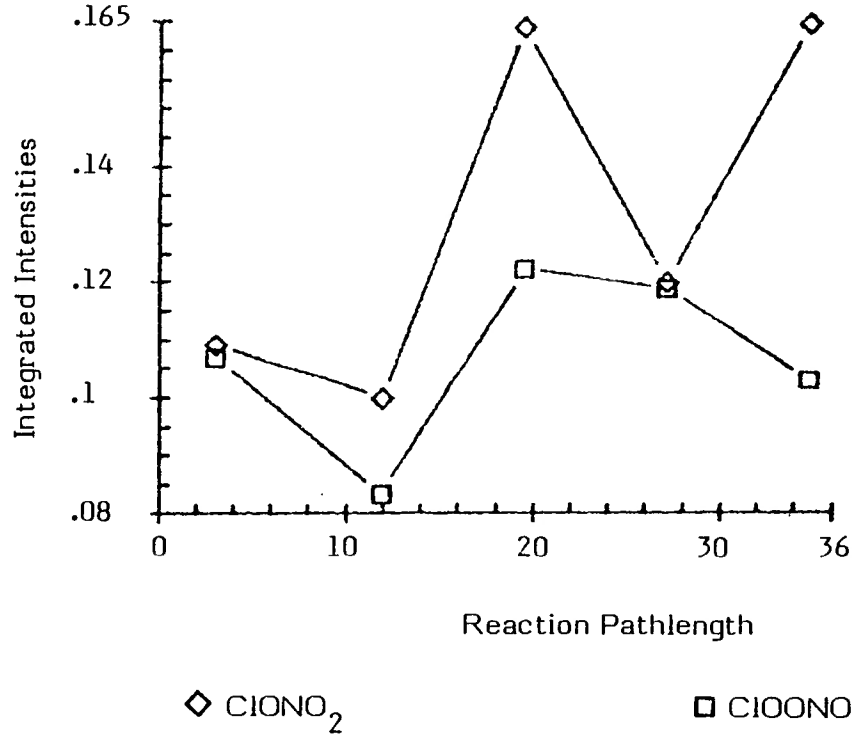


Fig. 3-7. Plot of integrated intensities of $ClONO_2$ and ClOONO against reaction pathlength in Cl + Cl_2O + $\overline{NO_2}$ (+M) reaction.

Table 3-4. Observed Infrared Energy (cm^{-1}) of Species in the Gas-Phase Reaction of $NO_2 + O_3$ (+M).[a]

ENERGY (CM^{-1})	SPECIES
2101.3	
1846.9	Iso N_2O_3
1837.5	N_2O_3
1728.1	N_2O_5
1718.8	N_2O_5
1650.0	N_2O_4
1631.3	N_2O_3
1615.6	NO_2
1606.3	--
1600.0	N_2O
1368.0	--
1300.0	N_2O_4
1284.4	N_2O
1271.9	N_2O_4
1046.9	O_3
909.4	Iso N_2O_4
793.8	Iso N_2O_4
756.3	NO_2
709.4	O_3

a. S. Vijai, S. C. Bhatia, and J. H. Hall, Jr., Unpublished Work (1981).

A careful study of the gas-phase reaction products of chlorine atoms with O_3 and NO_2 (Fig. 3-8) shows absorptions similar to those observed in Fig. 3-2. There are four peaks in the 1700 - 1740 cm^{-1} region, these are 1739 cm^{-1} (a shoulder), 1731 cm^{-1}, and a doublet at 1722 cm^{-1} and 1716 cm^{-1} (Table 3-5), and within the experimental error, are in agreement with the 1736 cm^{-1} (a shoulder), 1727 cm^{-1}, and the doublet at 1719 cm^{-1} and 1714 cm^{-1} observed in the reaction of Cl_2O + Cl + NO_2 (+M). The absorption at 1731 cm^{-1} is close to the observed 1727 cm^{-1} peak in the matrix-isolated spectrum of synthesized $ClONO_2$ (Chapter II) and in the spectrum of the gas-phase reaction of Cl + Cl_2O + NO_2 (+M). Hence the 1731 cm^{-1} absorption can be attributed to the N=O stretch in $ClONO_2$. The absorptions of NO_2 asy-stretch at 1288 cm^{-1}, ClO stretch at 809 cm^{-1}, NO_2 scis. at 789 cm^{-1}, and NO stretch at 564 cm^{-1} further confirm the presence of $ClONO_2$. Absorptions close to these were also observed in the spectrum of synthesized $ClONO_2$ and in the spectrum of ClO + NO_2 (+M) reaction (Chapter II). For the same reasons given in the last Chapter it is difficult to assign either the 1722 cm^{-1} or the 1716 cm^{-1} absorptions to ClONO which is a product of the gas-phase reaction of Cl + NO_2 (+M) (Chapter I). However it is certain that both ClOONO and $ClONO_2$ are present in the 1700 - 1740 cm^{-1} spectral region. The results of the NO_2 + O_3 (+M) reactions show some absorptions that might conflict with our assignments, but these absorptions have been assigned to the nitrogen oxides (Table 3-4).[8] This further confirms the fact that the absorptions in the 1700 - 1740 cm^{-1} region are due to the N=O stretch.[9] Thus the absorptions at 1722 cm^{-1}, 1288 cm^{-1} and 789 cm^{-1} are assigned to the N=O stretch, NO_2 asy-stretch, and NO_2 scis. respectively. And considering the O_2NO absorptions in Table 3-6, the absorptions at 911 cm^{-1}, 564 cm^{-1}, and 445

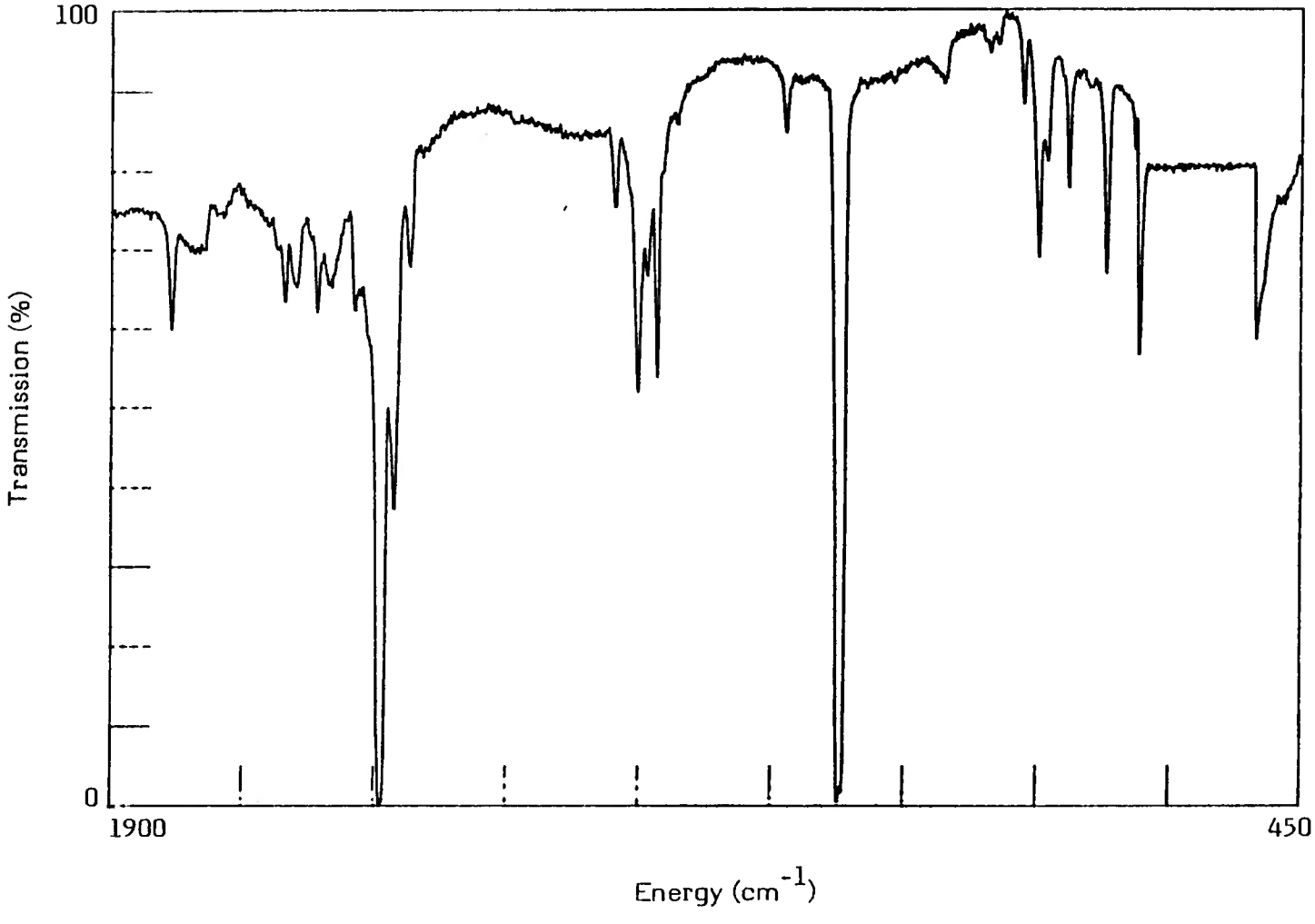


Fig. 3-8. The IR spectra of the gas-phase reaction products of chlorine atoms with pure $^{16}O_3$ and NO_2.

Table 3-5. Observed Molecular Vibrational Energy (cm^{-1}) for $ClONO_2$ and ClOONO Produced in the Gas-phase Reaction of Cl + $^{16}O_3$ + NO_2 (+M).

$ClONO_2$		ClOONO	
Energy (cm^{-1})	Vibrational Mode	Energy (cm^{-1})	Vibrational Mode
1730.7	NO_2 asy-stretch	1739.4	N=O stretch
1287.6	NO_2 asy-stretch	1722.1	N=O stretch
809.4	OCl stretch	910.7	N-O stretch
788.8	NO_2 scis.	850.1	--
563.8	NO stretch	563.8	ONO bend
421.9	NO_2 rock	445.1	OON bend
267.6	OCl bend	432.6 or 421.9	ClO stretch

Table 3-6. Vibrational Energy of O_2NO.[a,b]

ENERGY (CM^{-1})	VIBRATIONAL MODE
1845	N=O stretch
955	N=O stretch
1400	O-O stretch
540	ONO bend
454	OON bend

a. W. A. Guillory and H. Johnston, J. Chem. Phys., 42, 2457 (1965).

b. S. C. Bhatia and J. H. Hall, Jr., J. Phys. Chem., 84, 3255 (1980).

cm^{-1} are assigned to the N-O stretch, ONO bend, and OON bend respectively in ClOONO. The isotopic shifts observed when $^{18}O_3$ (Fig. 3-9) was used are 4.4 cm^{-1}, 3.8 cm^{-1}, and 3.7 cm^{-1} (Table 3-7) for the isotropic NO_2 asy-stretch, and NO_2 scis. respectively.

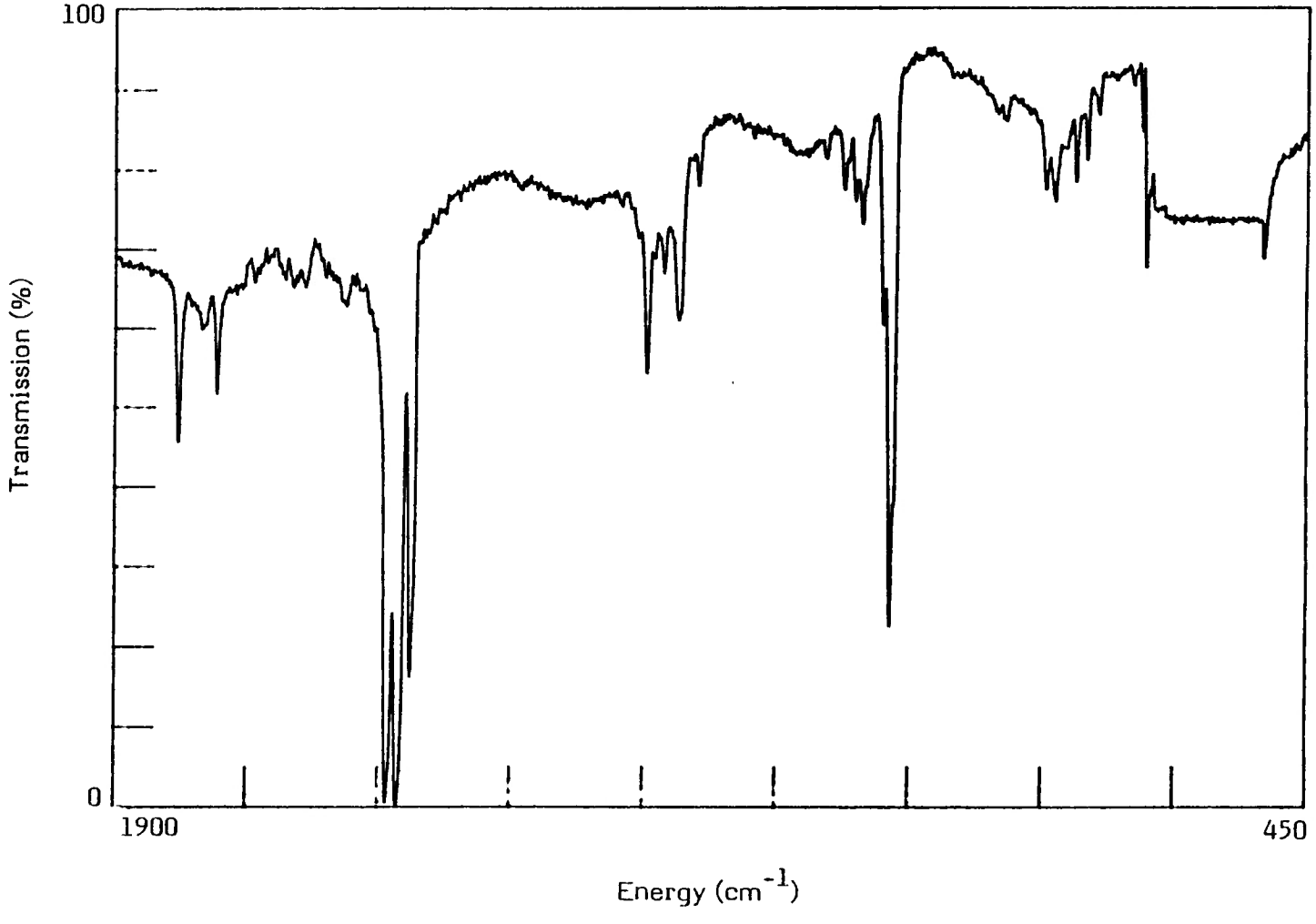


Fig. 3-9. The IR spectra of the gas-phase reaction products of chlorine atoms with pure $^{18}O_3$ and NO_2.

Table 3-7. Observed Molecular Vibrational Energy (cm^{-1}) for $ClONO_2$ and ClOONO Produced in the Gas-Phase Reaction of Cl + $^{18}O_3$ + NO_2 (+M).

$ClONO_2$		ClOONO	
Energy (cm^{-1})	Vibrational Mode	Energy (cm^{-1})	Vibrational Mode
1726.3 (4.4)	NO_2 asy-stretch	1736.3 (3.1)	N=O stretch
1283.8 (3.8)	NO_2 asy-stretch	1715.1 (1.2)	N=O stretch
773.2 (36.2)	OCl stretch	--	--
785.1 (3.7)	NO_2 scissoring	835.1 (15)	--
567.6 (-3.8)	NO stretch	567.6 (-3.8)	ONO bend
--	--	--	--
266.3 (1.3)	OCl bend		

CONCLUSION

It is clear from this work that in both the Cl + Cl_2O + NO_2 (+M) and the Cl + O_3 + NO_2 (+M) reactions, two identificable isomers ($ClONO_2$ and ClOONO) are formed. The appearance of the OClO peak means that (3-2) or (3-3), or both might be taking place, but since we have not been able to make any identification as to that effect, it is only reasonable at this point to assume that the reactions Cl + Cl_2O + NO_2 (+M) and Cl + O_3 + NO_2 (+M) proceed along two pathways, addition of the oxygen of the ClO radical to the nitrogen of NO_2, and addition of oxygen of the ClO radical to one of the oxygens of NO_2. The atmospheric implications of these reactions is that chlorine nitrate will act as holding tank for stratospheric chlorine due to its slow solar photodissociation rate. In contrast, ClOONO being a nitrite will decompose considerably faster in the stratosphere and we can assume that it will play at most a minor role as an inert chlorine reservoir in the stratosphere, although it might be involved in some catalytic cycle if its photolysis products are species other than ClO and NO_2.

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9. W. F. Fateley, H. A. Bent, and B. Crawford, J. Chem. Phys., 31, 204 (1959).